PHD

Wastewater minimization under uncertain operational conditions

Al Radwan, Suad A.

Award date:
2005

Awarding institution:
University of Bath

Link to publication

Wastewater Minimization under Uncertain Operational Conditions

Suad A. Al Radwan

A thesis submitted for the degree of Doctor of Philosophy

University of Bath
Department of Chemical Engineering

March 2005

TABLE OF CONTENTS

Index of figures

Index of tables

Acknowledgement

First and foremost, praise be to God, without whose care nothing could be achieved.

I wish to take this opportunity to express my deepest gratitude to Professor Barry Crittenden for his inspiring comments, valuable advice and unfailing support throughout the life of this research. I have benefited immensely from his research experience. I thank Dr. Haitham Lababidi for his continuous support and guidance. I also thank him for his valuable advice, in particular his suggestion to include stochastic optimization model and his immense help in GAMS programming.

I also wish to thank the numerous friends in the Chemical Engineering Department of Kuwait University and Bath University for directly or indirectly supporting this work. I wish to thank Kuwait University authorities and library staff for allowing me to access the literature.

I would like to express my utmost gratitude to my parents for their constant encouragement.

Last but not least, I am much indebted to my husband for his patience, care and constant encouragement and for the time to spare.

ABSTRACT

This thesis addresses the problem of uncertainty in optimizing water networks in process industries. Due to the fact that wastewater flow rates as well as the levels of contaminants may vary widely as a result of changes in operational conditions and/or feedstock and product specifications, optimal wastewater network designs should be resilient and able to accommodate such changes.

Uncertainties considered in this study are derived from actual operational practice of major water-using units in a typical oil refinery of 400,000 barrels/day throughput. Rather than directly varying the concentrations and mass loads, seasonal effects have been considered in this research to illustrate applications of the models.

Sensitivity analyses reveal that introducing uncertainty in operating conditions results in considerable changes in the connectivity of the units involved in wastewater reuse. The proposed stochastic optimization model produces a flexible wastewater network which is capable of accommodating uncertainties in operating temperature. In the presence of uncertainties, the optimal network minimizes the impact on the reuse connectivity (topology) by providing 32.2 tonne/hr of freshwater in addition to the condensing steam. The stochastic approach adopted in this research has been found to be effective in handling uncertainties and has resulted in flexible and resilient wastewater networks with low expected value of perfect information (EVPI).

Keywords: Wastewater minimization, Uncertainty, Optimization, NLP, Stochastic programming.

ABBREVIATIONS

AI	Artificial Intelligence
ARD	Atmospheric Residue Desulphurizer
ASU	Amine Sweetening Unit
BPD(bpd)	Barrels Per Day
CDU	Atmospheric Crude Distillation Unit
CFC	Chorinated Fluoro Carbon
CNS	Constrained Nonlinear System
CUT	Caustic Treating
DES1	Desalter I
DES2	Desalter II
DIS	Distillation
DNLP	Non Linear Programming with Discontinuous Derivatives
EVPI	Expected Value of Perfect Information
FCCU	Fluid Catalytic Cracking Unit
FW	Fresh Water
GAMS	General Algebraic Modelling System
GCC	Gulf Co-operation Council
GEN1	Regenerator
GOD	Gas oil Desulphurizer
GPM(gpm)	Gallons Per Minute
HCR	Hydrocracker
HDS	Hydro Desulphurizer
HTU	Hydrotreating Unit
IAC	Industrial Assessment Centers
KD	Kerosene Desulphurizer
LCA	Life Cycle Assessment
LP	Linear Programming
MCP	Mixed Complementary Problem
MILP	Mixed Integer Linear Program
MINLP	Mixed Integer Non Linear Program
MIP	Mixed Integer Program

MX1	Sweetening (Merox I)
MX2	Sweetening (Merox II)
NLP	Non Linear Program
NOx	Oxides of Nitrogen
OP(1)	Operations (1)
OP(2)	Operations (2)
OP(3)	Operations (3)
P&IDs	Piping and Instrumentation Diagrams
PPM(ppm)	Parts Per Million
QP	Quadratic Program
RMIP	Relaxed Mixed Integer Programming
SAA	Shuaiba Area Authority
SIMSCI, PROII	Simulation Sciences Inc, Process Simulator
SMART	Save Money and Reduce Toxics Program
SOx	Oxides of Sulphur
SS	Steam stripper of Crude distillation Unit
TGT	Tail Gas Treating
VDU	Vacuum Distillation Unit
WAP	Wastewater Allocation Planning
WRAP	Waste Reduction Always Pays

Chapter One

1. INTRODUCTION

The most serious challenges facing the chemical industries in the new millennium are their impacts on the environment. The enormous amount of industrial waste coupled with the growing awareness of the consequences of discharging effluents to natural resources has spurred the process industries to become more environmentally conscious and adopt a more proactive role.

Currently, environmental protection is a subject of global concern, and complex environmental regulations exist and continue to evolve in many countries (Mitchell-Fox, 1995). For instance, the US Environmental Protection Agency has mandated the Clean Water Act and Pollution Prevention. Other countries prohibit disposal of water that has been in contact with processes, products, or raw materials into natural waterways from industries like refineries and petrochemical plants. In fact, sustainable development of such industries necessitates the preservation of the environment. Industries create a demand not only for waste receptive services from the environmental media (air, forests, land and water) but also for some material inputs supplied by the environmental resources (for example wood in the paper and pulp industry). Environmental resources can ensure a sustainable supply of these services, if they are preserved at their natural regenerative level or the demand for waste receptive services is equal to the waste assimilative capacity of environmental resources (Murty and Kumar, 2000).

1.1. Need for Waste Minimization

Over the past two decades, significant efforts have been made to reduce the quantity of industrial wastes generated. Mulholland and Dyer (2001) & Crittenden and

Kolaczkowski (1994), defined waste as an unwanted by-product or a damaged, defective or a superfluous material from a manufacturing process. A secondary source of waste is the excess energy required to process and to treat any waste generated. Although some amount of waste generation is inevitable from manufacturing facilities, the availability of abundant treatment and disposal capacity for industrial waste can act as a disincentive for businesses to look for ways to improve the efficiency of their plants and to reduce waste generation at source. Underwood (1994) emphasised that the best time to attempt source reduction is before companies invest in treatment facilities and not after. This approach will avoid the need to manage the waste through costly means of recycling, treatment or storage. It is a preventive approach. It also usually involves simple technologies, as well as improved product yield and product quality that conserve natural resources.

According to Hollod and McCartney (1988), any company that has an economically and environmentally acceptable plan for waste management may well be the lowest cost producer. Reducing the generation of waste and improving the overall efficiency of the manufacturing process are fundamental to all successful chemical businesses.

In recent years the focus has shifted from downstream pollution control (end-of-pipe treatment) to a more proactive practice of trying to prevent pollution at the source of its generation, i.e., it is preferable to reduce wastes so as to help in reducing the waste disposal or processing costs. It also helps in reducing pollution and saves on money spent for waste disposal. Maunder (1999) and Oliver (1995) have carried out extensive work in this field and have proved with statistics that waste minimization leads to a reduction in pollution, which ultimately results in significant cost savings. It also improves working conditions, which adds to employee morale. It also improves the surrounding environment, which helps to ensure a pleasant neighbourhood and makes companies more attractive to customers and stakeholders.

One major pollutant generated by almost all process industries is wastewater. Water is vital in a number of processes. It is one of the most abundant material available in the world. It may be used as a heat sink and a heat source as well as a medium for extracting impurities from process streams. Hence it is important to consider wastewater minimization as part of any pollution prevention activity.

Water is also becoming an increasingly scarce commodity in Gulf Co-Operation Council (GCC) countries and it is now becoming a potentially limiting factor for agriculture and even for industrial development. The greatest challenge that the GCC countries are facing is the supply of fresh water to domestic, agricultural and industrial consumers. With over-exploitation of ground water resources and limitations in the desalination plants, planners are continuously searching for additional sources of water which can be effectively and economically utilized for further development.

Fresh water consumption in Kuwait is increasing at an average rate of about 6% in the last five years and the water production for the year 2002 was about 95 billion imperial gallons. The cost of producing such water is also high at the rate of about 10 US$/1000 Imperial Gallons (IG), compared to natural sources.

Hence, recycling/reuse of treated wastewater is one of the most important alternatives that can be used to reduce pollution and overcome the water supply problem. In GCC countries wastewater minimization should be given the highest priority in efforts to seek non-conventional sources of water that can be utilized to supplement the ground water and desalinated water. In fact, wastewater minimization has a great potential to play an important role in water resource management and to lessen the demand versus supply imbalance. Liu et al., (2004) have presented available tools for water system optimization such as water pinch analysis, graphical tools for water pinch, mathematical optimization, etc.

Even though many different types of waste are produced from refining operations which includes particulates, oxides of sulphur (SO_x) and oxides of nitrogen (NO_x), liquid effluent, organic chemicals, etc., the main pollutant from a refinery is wastewater.

1.2. Wastewater in Refinery Operations

A refinery is a principal industrial water consumer and hence its water is one of its main sources of pollution. Refinery facilities consist of sophisticated networks of process units which are generally integrated to reduce the processing cost. These units interact with each other depending on the unit operations needed and the final economic requirement of the product slate.

As per the published document 'Profile of the Petroleum Refining Industry" by USEPA (1995), wastewater from petroleum refining consists of cooling water, process water, storm water, and sanitary sewage water. A large portion of water used in petroleum refining is used for cooling. Most cooling water is recycled many times. Cooling water typically does not come into direct contact with process oil streams and therefore contains less contaminants than process wastewater. However, it may contain some oil contamination due to leaks in the process equipment. Water used in processing operations also accounts for a significant portion of the total wastewater. Process wastewater arises from desalting crude oil, steam-stripping operations, pump gland cooling, product fractionators, reflux drum drains, cooling tower blow down and boiler blow down. Because process water often comes into direct contact with oil, it is usually highly contaminated. Storm water (i.e., surface water runoff) is intermittent and will contain constituents from spills to the surface, leaks in equipment and any materials that may have collected in drains. Runoff surface water also includes water coming from the roof drains of crude and product storage tanks.

As indicated in Table 1.1, the quality of wastewater generated from different process units varies very widely, depending on the feed source and process requirements. There is no single treatment that is cost effective to handle the entire spectrum of wastewater generated in a refinery. Due to this diversity of waste sources and quality, the environmental impact of such facilities cannot be mitigated simply by end-of-pipe treatment of the generated waste. This might not be the most cost-effective option.

Table 1.1: Design Quality of Sour Water streams generated from typical refinery units.

Unit	Impurities (wt ppm)	
	Ammonia	H_2S
Crude Distillation	259	89
Atmospheric Residue Desulphurizer	27158	41660
Kerosene Desulphurizer	198	379
Gas Oil Desulphurizer	884	3331
Vacuum Distillation	70	99
Hydrocracker	12627	25700
Tail Gas Treater	1152	1514

A more constructive approach is to integrate the process units to reduce the quantity of wastewater and improve its quality. Another better and more challenging approach is to reduce waste generation at source by making changes and modifications to conditions in the unit operations such as temperature, pressure, partial pressure, and catalyst type.

1.2.1. Sources of Process Wastewater

A common simplified water flow diagram for a typical process industry is shown in Figure 1.1. Process wastewater sources fall into the following three major categories:

a) Wash water generated from washing impurities.

b) Wastewater produced as a by-product of process operations such as converting the hydrogen sulphide into sulphur, desalting, steam for stripping, etc.

c) Wastewater as a by-product of utility water use (e.g., blow down from boilers or cooling water systems).

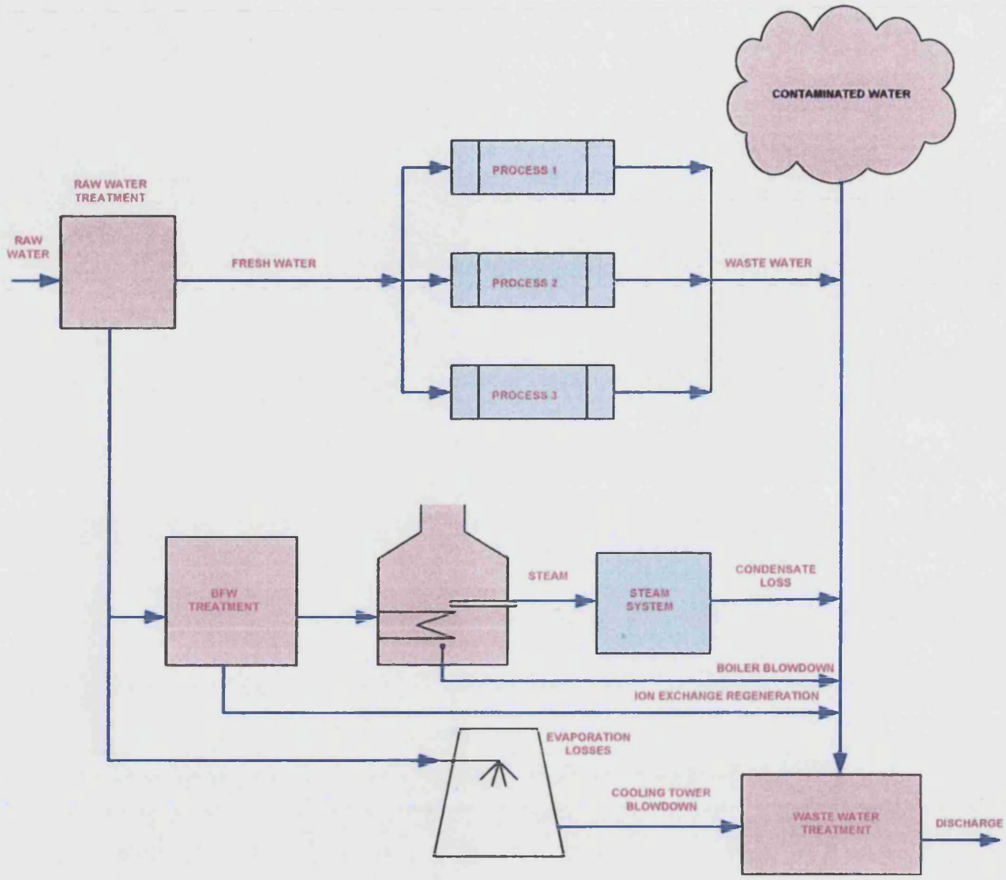


Figure 1.1: A typical water flow diagram in a process industry

1.2.1.1 Wastewater Generated from Washing Impurities

In an oil refinery, wastewater is produced from the washing of hydrotreater effluent streams. Water is used in hydro processing units such as the atmospheric residue desulphurizer (ARD), the hydro cracker (HCR), the kerosene desulphurizer (KD) and the gas oil desulphurizer (GOD), in order to avoid the build up of ammonium salts in down stream reactor system which cause corrosion, leading to leakage in the lines. Water is used also in the fluidized catalytic cracking unit (FCCU) for washing the ammonium and cyanide salts in the overhead stream.

Crude oil contains certain dissolved salts and the salt concentration is to be reduced to the minimum for the same reasons cited above. Hence, washing of salt with water is carried out in a desalter operation and this operation generates wastewater. This type of wastewater generation (i.e., the intentional addition of water to remove contaminants) is typically characterized by the requirement to remove a fixed amount of one or more contaminants (e.g., salt in a crude oil desalter). In the desalter, the wastewater (brine) contains some oil, which is an undesirable but inevitable consequence of contacting oil and water. It is the bulk concentration of the oil in the wastewater, rather than the absolute quantity, that is typically constant for a steady desalter operation.

1.2.1.2 Wastewater Produced from Strippers

In some cases wastewater is generated by process operations in which water is added for process reasons other than to remove contaminants. This typically results in a fixed mass flow of secondary water, with contamination from process concentrations. The flow and the composition are functions of process operating conditions, which generally cannot be changed, as this would have commercial implications. However, in some cases, the regenerated water can be used in place of fresh water in operations that do not require pure water.

1.2.1.3 Wastewater from Utility System

Wastewater is also generated due to the concentration of trace impurities such as blow down from utility units including boilers and cooling towers. This wastewater arises because the makeup water has to be added to the utility system in order to replace, for example, evaporative losses from cooling towers, steam losses (due to leaks and live steam injection), and condensate losses from steam systems. These losses are essentially pure water, so in the absence of a blow down the contaminants from the makeup would concentrate to unacceptable levels within the utility system. Chemicals (e.g., biocides) are also commonly added to water within utility systems, and the blow down stream inevitably contains some of these materials.

1.3. Wastewater Minimization Options

There are basically three wastewater minimization options; water reuse, regeneration and reuse, and regeneration and recycle.

a) Reuse

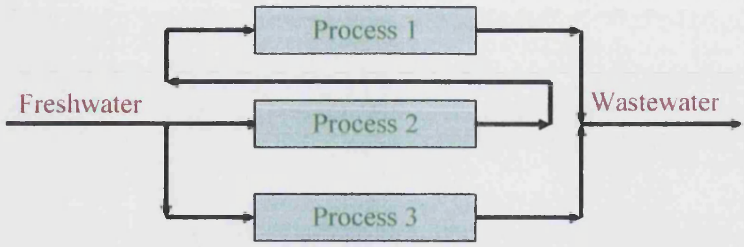
Wastewater product from one unit can be fed to another unit rather than using fresh water (Figure 1.2a). A typical example of water reuse in a refinery operation is using part of the wastewater generated from the vacuum tower, the gas oil desulphurisation unit or the kerosene desulphurisation unit as washing water in other units without any treatment. Another example is using the blow down water from boilers as makeup water to cooling towers without any treatment.

b) Regeneration & Reuse

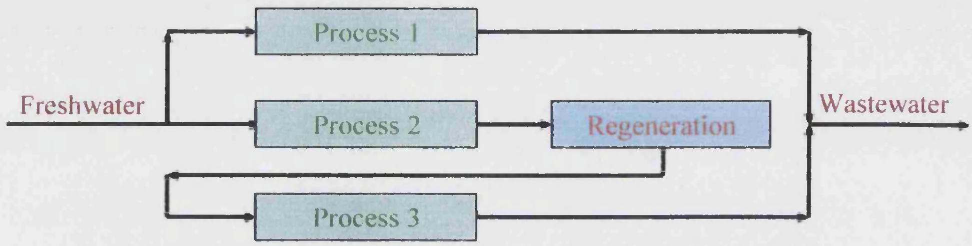
In this case, contaminated water from one process is partially treated to make it suitable for use in one or more of the water-consuming operations (Figure 1.2b). Treated water should not be used in the same unit to avoid impurity concentration.

There are many different types of regeneration equipment, such as sour water strippers, filters, membrane separators, and ion-exchange processes. The objective of such processes is to remove contaminants to make the water stream suitable for reuse or recycle, or even to render it for end of pipe treatment.

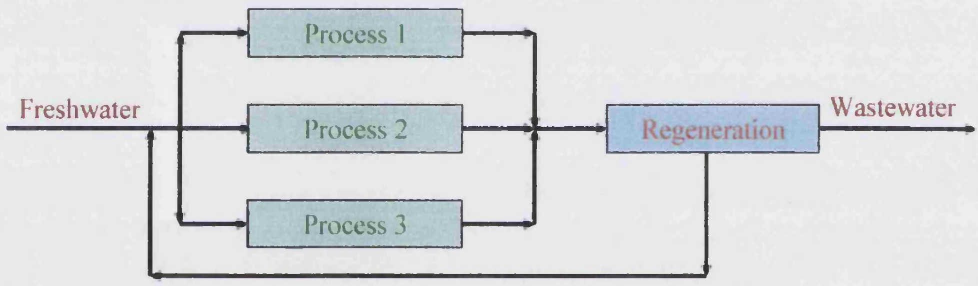
As an example, treated sour water can be used as a feed to the desalting unit to remove salts from the crude oil. Other examples are using regenerated water in hydrodesulphurization and hydrocracking units as well as in the FCC unit.



(a) Water reuse



(b) Water regeneration and reuse



(c) Water regeneration and recycle

Figure 1.2: Wastewater minimization options.

c) <u>Regeneration & Recycle</u>

In this case, contaminated water is treated and recycled back to the same unit (Figure 1.2c). When recycled water goes back to the same process, contaminants that are not removed during regeneration would get concentrated, leading to unacceptable levels (process conditions). Reuse targets can be useful in cases where built-up trace contaminants that are not removed in regeneration would be problematic. However, this can be mitigated to a large extent by using the regenerated water in as many units as possible.

As an example, the sour water from the ARD unit can be sent to a regenerator and the regenerated water used in more units such as the KD, ARD and the GOD.

As detailed earlier, chemical and petrochemical industries use substantial amounts of water. Wastewater streams containing several contaminants such as phenols, sulphides, ammonia, benzene, oil, etc., create environmental pollution problems (Bagajewicz and Savelski, 2002). Hence, a considerable amount of the fresh water requirement in a typical refinery can be minimized by applying the regeneration/recycle/reuse options on the wastewater network. This will minimize wastewater discharge to environment as well.

1.4. Wastewater Minimization Mathematical Modelling

Over the past few decades, development in the field of mathematical optimization has been quite fast. The main function of optimization is to maximize the objective function based on identifying the vectors that maximize/minimize the objective function subject to constraints. When all variables and objective functions are linearly variable then it is called a linear programme (LP). When some of, or the entire set of variables are not linearly variable then it is called Non Linear Programming (NLP).

In order to study the feasibility of water minimization options, it is essential to construct a typical industry-wide wastewater network. This network should include all major unit operations in the chosen industry. Information is required about water demand, inlet and outlet concentrations and temperatures, impurities involved and their concentrations, and any constraints restricting water reuse. Once the wastewater network has been finalized and all data related to the required parameters have been collected, then a mathematical model may be developed and used to select the optimal approach to wastewater minimization. Methods might be based on non-linear programming (NLP) and mixed integer non-linear programming (MINLP) techniques (El-Halwagi, 1994).

While many opportunities are available for pollution prevention in refinery operations, the work described in this thesis will focus on wastewater minimization under uncertain operational conditions, as detailed in 1.4.1 below. In particular, this thesis discusses the recycle/reuse option for sour water generated in a typical refinery. In order to have a better understanding about the sources of sour water generated in a refinery, it is prudent to give some details about crude oil and refinery operations. Accordingly, a brief overview of a typical refinery is given in Appendix A.

1.4.1. Uncertainties

Refineries consist of complex integrated units. Due to economic and marketing reasons, units are operated under different modes such as different operating temperatures and pressures (e.g. production of aviation turbine fuel or gas oil from the hydro cracker unit). Some units are shut down or operated at different capacity to increase the overall profitability of the refinery due to economical and logistical reasons. Processing different type of crude oils also increases the variability and uncertainty.

For the above reasons, pollutants produced from refinery units are changed frequently such that both the quantity and quality of waste waster produced can be variable. Hence, any solution proposed for wastewater minimization must take these uncertainties into account.

1.4.2. Wastewater Network Models

Having defined the terminologies used to reduce wastewater generation by improving the recycle/reuse of generated wastewater and to reduce discharge to outside sources, the next step is to develop a mass balance model for impurities or contaminants. In order to create this model the quantity of wastewater generated from each unit needs to be measured. The quality with respect to various contaminants also needs to be measured. Then a typical refinery-wide wastewater network can be drawn indicating the flow rates and concentrations for each stream. This network model must include all refinery unit operations, as well as water demands, inlet and outlet concentrations of the impurities involved, and any constraints. The model should clearly indicate the total pollutants from the system and the maximum allowable pollutants for each of the recycle/reuse streams. The type and capacity of units which can remove pollutants (together with any constraints), should also be represented in the network.

All this information then provides a basis for defining appropriate wastewater streams, thereby providing a convenient basis for defining appropriate options for recycling or reusing each stream collectively or independently. Considering the number of refinery process units, the number of pollutants and their potential for recycle and reuse, this problem is a complex one, and hence the mass balance model cannot be solved manually. Some type of mathematical algorithm is required to find an optimum solution. Commercial optimization packages are available to obtain the following:

a) Target wastewater flow (minimized), i.e., aiming at reducing the design wastewater quantity that would be generated from an industry.

b) One possible process structure for achieving the target flow.

1.5. Wastewater Minimization Techniques

Research in process integration now covers a much wider area than energy conservation and the scope has broadened to include raw materials efficiency, emissions reduction and process operations (Smith.2000). The currently available techniques to meet the above objectives are:

a) Pinch Analysis Method

b) Non-Linear Programming Method

The Pinch technique analyzes chemical processes systematically with the help of the first and second laws of thermodynamics. A new systematic heat recovery design approach based on thermodynamics is proposed for water stream sets leading to energy pinch problems (Savulescu. et. al 2002). The mass balance and thermodynamics provides the equations for calculating the concentration changes in the streams passing through a process. The pinch defines the minimum driving force allowed in the process unit. The pinch point is the point at which the concentration gradient is the lowest.

The main difference between the Pinch and NLP techniques is that the mass-transfer pinch approach is basically a conceptual tool with a largely graphical output. It provides insights into design options that are not readily obtained in any other way. On the other hand, the NLP approach is basically a computational method. It yields a rigorous solution to an optimization problem, but gives few insights into design options. The NLP method provides the required output in a single step by generating both targets and a feasible design. However, pinch analysis follows a number of steps from targeting to the design of the network. Other differences between the approaches are highlighted in the following points.

a) Guarantee of an Optimal Solution

For any given set of data, the output of the mass-transfer pinch approach will be a guaranteed mathematical minimum based on the given assumptions. In contrast, nonlinear programming can only give a local optimum. Near global optimum or global optimum values can be achieved by providing good initialization for the key decision variables. Thereby the solution obtained by the NLP method is similar to the pinch method. Furthermore, sensitivity analysis can be done very easily.

b) Handling Multi-Component Problems

Another difference is in handling multi-component (contaminant) problems. The NLP approach can handle a large number of components and the results are easy to interpret. However the method requires powerful computers and a good computer software package. It is difficult to carry out multi-component analysis by the mass-transfer pinch analysis method. It can be even more difficult to interpret its results.

c) Handling Constraints

Non-linear programmes are designed specifically to use constraints. The practical unit constraints, or indeed any other limitations created by other process units, can be incorporated easily in NLP even though the solution is not thermodynamically the optimum. For example, the water flow from one unit can be diverted to another unit. However, this aspect is difficult with the mass-transfer pinch approach.

d) Handling Concentration Relationships

Concentration relationships can be easily defined in the NLP approach. Two good examples of concentration relationships are the fixed pickup model (fixed amount of impurities will be transferred to water, irrespective of inlet concentration and the process parameters) and the fixed bulk concentration model (the outlet concentration of water is fixed based on thermodynamic equilibrium). While the pinch-based approach can also handle almost any pickup relationship, it is difficult to implement.

e) Data Handling

Both of the above methods handle the data in different ways. The NLP approach treats all operations as discrete, indivisible entities but in contrast, the mass-transfer pinch approach treats operations as having continuous variations in composition between their inlets and outlets. Practically, all the unit operations are discrete. Therefore, having a continuous variation in composition may not lead to a much different solution. Nonetheless, indivisibility of operation in the NLP approach can be overcome by splitting the unit operations.

The design methods depend upon the way in which the data are handled. The pinch approach uses mass-transfer driving forces which require splitting of operations that may not be feasible in some cases. However, when regeneration is introduced, the splitting of operations may be necessary to achieve the target. The design can always be modified to add or remove the split by appropriately changing the water flow.

Each operation is treated as discrete and indivisible in the NLP method. Consequently, it requires little (if any) structural change to simplify the design. Based on the constraints, it is possible to split the unit operation to reach the optimum solution.

f) Setting Targets

The pinch method can generate water consumption targets for regeneration- reuse and regeneration- recycle very easily. It can easily handle the build up of traces of contaminants that are not removed in regeneration. On the other hand, in the NLP approach it is difficult to prevent recycle without introducing other (unintended) constraints. Nonetheless, the NLP model concentration build-up in recycle systems can be estimated so that most practical situations can be handled.

In the past, generic NLP solvers like GAMS have been used for solving water networks but are not completely user friendly. However, this has been overcome by the software design tool (WADO™) developed by Ullmer et al., of Siemens (2003) which uses Graphical User Interface (GUI) techniques. This tool is also based on mathematical programming (an LP model). This technique is still in the development phase.

Gerald et al., (2001) cautioned that it would be too venturesome to spend a lot of effort on wastewater minimization projects without knowing the potential savings in advance.

They also suggested that reuse designs are frequently criticized to be unrealistic as they neglect constraints given by existing equipment, the introduction of new hazards due to their complexity, and entailing extensive piping needs. Most of the wastewater reuse methods discussed in the literature only argue with concentration differences enabling integration. They neglect other equally important quality criteria used in process design and plant layout, such as safety, cost, operability, maintenance, appearance, piping and material flow.

1.6. NLP in Wastewater Minimization

Nonlinear programming provides a powerful means of quantifying the scope for wastewater minimization and identifying specific recycle and reuse arrangements to achieve the target. The method provides a rigorous solution for the minimum freshwater demand or wastewater generation rate in a production facility, and it can readily be incorporated in a user-friendly software package. The technique is particularly well suited to situations where some pre-screening of process options has already been carried out, and to identify appropriate regeneration options and process modification opportunities. Pre-screening can be accomplished with one of the other process integration methodologies, such as hierarchical review or mass-transfer pinch analysis. According to Rossiter and Nath (1995), industrial studies using this approach have typically identified opportunities to reduce water flow by around 30 percent.

Rossiter and Nath (1995) commented that NLP is more suitable for process industries like oil refineries. It has been shown that about 20~40 % reduction in freshwater intake and wastewater discharges is possible by using this approach.

A mathematical model has to be developed based on design data. Most of the data such as operating conditions (temperature, pressure) and mode of operation are fixed (determined) under steady state conditions and constraints are fixed based on the worst case. This model is known as a deterministic model. However in reality, process conditions are changing dynamically. Constraints and variables are thereby changing based on upstream unit economics. Therefore stochastic additions need to be incorporated in this deterministic model to make it suitable for real operation in the dynamic environment. This can be best done by developing a stochastic model.

1.7. Stochastic Programming

Stochastic programming supports decision making under uncertain conditions. It is a methodology for bringing uncertain future scenarios into the traditional decision making framework of linear programming. The profitability of many industries like aerospace, automotive, engineering, environment, manufacturing, refining, health care, transportation, travel, and weapons can be enhanced through implementation of stochastic optimization in design and control.

Just as linear programming models determine the optimal allocation of constrained resources to meet known demands, stochastic programming models use today's resources to meet future uncertain demands in such a way that the user can explore the trade off with respect to expected risks and rewards to make informed decisions.

In most industrial applications, however, all the information needed to formulate and solve a design or control problem is deterministic. However, the system is normally designed based on known conservative factors. Accordingly, the final solution is expected to be optimal and reliable, based on the conservative inputs.

In reality, uncertainty exists everywhere. Stochastic programming problems are required from applications with inherent uncertainty. In experiments, we may not know all the design parameters. In simulations, we may not know, or have perfect descriptions of the input parameters to computer-based models. Additionally, it is possible to have uncertainty within the computer-based models themselves.

By formulating optimal design and control problems so that uncertain information is reconciled, it may be possible to generate optimal solutions that are robust and reliable within some safety margin. Our goal is not only to formulate stochastic programming problems that intelligently "incorporate" uncertain information, but to develop robust and efficient stochastic programming methods that solve these problems.

Even though stochastic programming provides great modelling power and flexibility, users have to put in much effort, and many inputs of data corresponding to various uncertainties have to be incorporated. The size of the problem increases significantly. Accordingly, obtaining and analysing the solution is not easy.

1.8. Conclusion

It is essential to reduce all types of waste not only to meet environmental regulations but also to stay competitive in industry. Since water is a scarce resource in GCC countries including Kuwait and wastewater is a main pollutant from a refinery operation, this thesis deals with methods for minimizing wastewater generated from a refinery operation and thereby reducing the freshwater requirement. The novelty of this thesis is that it describes wastewater minimization under uncertain operating conditions using non linear programming, combined with a stochastic approach.

Chapter Two

2. LITERATURE SURVEY

Waste production is the inescapable result of manufacturing processes upon which current quality of life depends. The proper goal is to minimize waste generation from the industries that burden the environment. This is to be accomplished through implementation of an appropriate combination of source reduction, recycling, recovery, and treatment, with due consideration of economics and worldwide industrial competitiveness (Kosson, 1988). It is well understood now that pollution is a global issue with real impact on both environment and human health, and unless the huge output of industrial waste is reduced at source, humankind can expect little real improvement in the critical risk affecting the world environment and human life (Underwood, 1994; Oliver, 1995; Al-Muzaini, 1999).

Structured programs designed to improve energy efficiency, environmental efforts, and safety is not new concepts and can be tracked back to World War II (Drabkin et al, 1988). Enhancing environmental performance is currently an international quest, and minimizing the amount of hazardous waste generated has become a serious challenge to the process industries.

In spite of the advancement of treatment processes and technologies, end-of-pipe treatment clearly has proved to be unable to meet such challenges. The current trend in the process industries is pollution prevention through source reduction, a strategy which was initiated around fifteen years ago. The US Office of Technology Assessment stated back in 1986 that US National policy discourages waste generation and encourages practical source reduction and recycling, either by voluntary or legislative means (Kosson, 1988).

2.1. Waste Generation in Process Industries

The chemical process industry is faced with a need to manufacture quality products whilst minimising production costs and waste generation, at the same time complying with a variety of safety and environmental regulations (Dantus and High, 1996). Mulholland and Dyer (2001) define industrial waste as an unwanted by-product, or damaged defective or superfluous material from the manufacturing process. They also list the following three classes of waste that are normally produced by manufacturing processes:

a) Process wastes that are produced while transforming lower value raw materials into higher value products.

b) Utility wastes that result from utility systems which are needed to run the process; e.g., steam, electricity, water, compressed air, etc.

c) Other wastes that result from start-up and shutdowns, housekeeping and maintenance activities.

In short, waste generation represents the depletion of mostly non-renewable resources, and hence the basis of a responsible corporate attitude should be waste minimization and subsequent reduction of pollution at source (Laing, 1992).

In fact, there is no chemical process in which only the target product is manufactured. Other materials not desired by the manufacturer are also obtained in gas, liquid or solid states. These are often referred to as residues. Chemical production is thus a two-edged sword. On the one hand it manufactures products (the goods) and on the other hand it produces residues (the bads). Sometimes, these residues can be reused. If utilization is impossible for technical and economic reasons, then these residues become wastes (Christ, 1999).

According to Crittenden (2001), treatment and disposal are the final waste management options which should only be used once other avenues of prevention, minimization and recycling have been exhausted. All wastes and discharges must be treated in order to render them harmless. This is the lowest level in the hierarchy and does not merit the labels of clean technology.

2.2. Waste Minimization

According to Drabkin et al. (1988), waste minimization is a value management activity with the primary objective of reducing the quantity and/or the toxicity of production wastes in a manner consistent with the goal of protecting the environment and achieving corporate objectives. A waste minimization activity may be differentiated from an environmental audit programme, in that it does not seek to determine or improve the regulatory compliance status of a facility, but rather, is primarily oriented towards producing a set of effective measures to reduce waste generation.

A waste minimization audit is a useful tool for reducing waste generation (Drabkin et al., 1988). This procedure allows an in-depth investigation and encourages creativity. The result of such an audit program is not only good for the environment but also contributes to financial savings. Maunder (1999) claimed that an effective waste minimization policy in most companies could reduce operating costs by at least 1% of turnover without too much effort or cost. Oliver (1995) cited several examples and explained that reduction of waste not only reduces pollution but also improves plant efficiency thereby conserving raw material and utilities. Rice (1988) gave details about reducing wastes by 10%, which would yield substantial savings in waste disposal costs. When that 10% is compounded with annual waste disposal- costs, the saving on waste disposal increases by 25-50%, and the potential return on investment becomes even greater. Such a reduction in a unit's operating cost can turn a loss-making process into a profitable activity.

With the level of saving going straight to the bottom line in financial accounting no one can afford not to look seriously at waste minimization within their company. Waste minimization also improves working conditions, which adds to employee morale. It also improves the surrounding environment, which makes for a pleasant neighbourhood and makes companies more attractive to customers and stakeholders (Maunder, 1999 and Oliver, 1995).

Boden (1997) states that "... what you don't measure, you can't control - so waste generation shall be monitored similar to electricity systems." It is well recognised that waste from the chemical industries can be minimized in at least four general ways

(Underwood, 1994; Camm and Nuttall, 1995; Dantus and High, 1996; Hollod and McCartney, 1988; Al-Muzaini, 1999):

a) By modifying the process to minimize waste generation.

b) By recycling waste preferably into the process in which it is generated.

c) By converting waste in to useful and valuable by-products.

d) By changing the waste's nature to make it less toxic and voluminous for ultimate disposal.

Fromm et al. (1987) emphasized that reducing or avoiding waste generation is the most desirable goal, and should be attempted first. Then comes the recycling and treatment approaches. Flower et al. (1995) and Nelson (1999) have listed process changes that facilitate waste minimization. Based on their work, the following has been developed for typical refinery applications.

	Required process change (Flower(1995) and Nelson (1999))	Example	Benefit
1	By reducing the temperature	With better catalyst system the reactor inlet temperature can be reduced in units like HCR, ARD, etc.	Reduced overall energy consumption which reduces utilities consumption and hence reduced the utility waste
2	By reducing the pressure drop	By periodic cleaning of compressor suction strainers in rotating equipment	This will reduce overall pumping/compression costs resulting in reduced energy consumption.
3	By reducing the mixing of streams of different composition (this will reduce the inherent thermodynamic gradient).	Hot /cold feeds are not mixed to utilise thermal gradient available in the cold stream. ex. Preheat trains in crude distillation unit.	Reduced energy consumption.
4	By avoiding over sizing/under sizing the system	The surge control valve will be opened permanently in an oversized compressor.	Reduced steam / power consumption, which reduces waste generation.
5	By avoiding reprocessing and increasing the conversion to desired products.	By using desired catalyst, unconverted oil will not be produced from HCR which will avoid reprocessing at FCC	Reduced operating cost and additional production of more valuable product.

It is to be noted that identifying a problem does not always mean a solution is forthcoming, but once an opportunity is recognised, finding a cost effective solution is frequently straightforward (Nelson, 1999).

Chang (1996) stated that during the past several decades, the use of integration techniques as design tools to minimize the operating and capital cost of chemical plant has matured considerably, and is now common practice in process industries. As a result of serious concern about the environment, process synthesis methods for waste reduction are of growing importance. These aspects were also emphasised by Fromm et al. (1987) and Laing (1992). They list the incentives for reducing waste generation as:

i) A desirable environmental goal.

ii) Can reduce a firm's potential liability for problems associated with offsite activities.

iii) Enhances waste handling and disposal.

In order to take advantage of the incentives of waste minimization, the chemical industries are focusing on two ways of solving the problem:

i) Design completely new processes and effectively start again; i.e., reduce waste generation at source by good design.

ii) Optimize the current process with a waste reduction approach integrated with "end-of-pipe" treatment.

The first approach will inherently be able to generate better solutions than the second because new technologies, recycling waste streams and equipment alternatives can be accommodated more easily. Brief details about both these approaches are given below.

2.2.1. Waste Minimization through Source Reduction

Source reduction technology, where waste streams are reduced or eliminated by modification of input material, or good housekeeping practices, are some of the most effective means of minimising waste (Flower et al., 1995). It is clear that these changes are best included within a process at the early stages of design (during process synthesis) rather than by process modifications later on. This type of source reduction activity could pave the way for impressive savings within chemical plants and for a more environmentally friendly industry (Underwood, 1994). Clearly, the best answer to source reduction is not generating waste in the first place, thereby avoiding the need to manage it through costly means such as recycling, treatment or storage.

The increased concern over air and water quality, government regulations related to emissions, escalating treatment costs as well as the increased risk of liability are driving industries to develop and apply new technologies to achieve waste minimization through source reduction efforts (Jandrasi and Masoomian 1995). In such a situation, the end of pipe treatment approach is no longer feasible or recommended (Dantus and High 1996). While minimization of waste at source is the most desirable, it is nonetheless, often the most difficult way to reduce waste (Hollod, and McCartney, 1988).

Even though government regulations create motivation for compliance, Jandrasi and Masoomian (1995) comment that waste formation is often associated with process inefficiency. In other words, time and effort devoted to pollution prevention often has a positive financial impact on environmental, process and business objectives. Companies with an economically and environmentally acceptable plan for waste management may well be the lowest cost producers (Hollod and McCartney 1988). Reducing the generation of waste and improving the overall efficiency of the manufacturing process are fundamental to all successful chemical businesses. Even though waste minimization may cost the companies in the beginning, Laing (1992) believed that it is ultimately part of a sustainable development and therefore an investment in the future.

Although some amount of waste generation is always inevitable from manufacturing facilities, Underwood (1994) believed that the availability of abundant treatment and disposal capacity for industrial waste acts as a disincentive for businesses to look for ways to improve the efficiency of their plants and reduce waste generation before it happens. Thus, the time to attempt source reduction is before companies invest in treatment facilities and not after. This approach will avoid the need to manage the waste through costly means of recycling, treatment or storage. It is a preventive approach. It also usually involves simple technologies, improved product yield and product quality that conserves natural resources.

The US industries SARA (Super Fund Amendments and Reauthorization) indicated that a change in philosophy was necessary and emphasised the priority on source reduction. The same idea was expressed by Comell and Rittmeyer (1990) and the US EPA (1990).

2.2.2. Waste Minimization through Waste Reduction

Considering the advantages of waste minimization, Camm and Nuttall (1995) expected that waste minimization will replace/reduce end of pipe treatment in the coming years. This view was also shared by Al-Muzaini (1999). Papalexandri et al. (1994) emphasised that the movement away from end of pipe treatment technologies towards waste minimization and mass efficient processes has become an important alternative in waste management along with process design towards minimum waste generation.

According to Dantus and High (1996), waste minimization is defined as the reduction, to the greatest extent possible, of hazardous pollutants that are generated and subsequently treated, sorted or disposed.

Rossiter and Spriggas (1993) explained that systematic techniques are developed to identify process improvement opportunities. They present a systematic method for minimising waste generation such as the total site pinch method, hierarchical review, and cost modelling method. These methodologies are further explained by Linhoff et al (1994), Rossiter et al. (1991) and Clift (1995). They can be used to explore the three-way trade off between capital costs, operating costs and environmental impacts.

Al-Muzaini (1999) presented the waste minimization efforts of the Shuaiba Area Authority (SAA), which accommodates most of the large scale industries and refineries in Kuwait. He outlined the steps followed to reduce waste generation at source and recommended that waste minimization efforts should include i) establishing corporate policies and practices, ii) identifying various techniques, iii) developing a database on the quantities of wastes generated, and iv) funding research projects which might lead to effective recycling and reuse programs.

Presently, there is no easy way to identify waste minimization techniques developed in one industry and then to apply them to another industry. Additionally, there is no technique which allows researchers to attack the problem at its source where changes will have the greatest impact on hazardous waste generation. Nevertheless, Morse et al (1994) explained that the problem could be broken down based on unit operation, configuration or process.

2.3. Wastewater Minimization

In the past, water has generally been considered to be limitless in availability and cheap. According to Linhoff and Smith (1994), this attitude is changing. Today's strong economic and regulatory factors are prompting many industries to place an increased emphasis on water conservation by adopting minimization of water use, reuse and recycling (Ross and Sasser, 1998). These factors include rising water costs, diminishing water supplies and increasing environmental regulations. When combined, the impact of these factors can have a dramatic effect on profitability (Nobel and Allen 2000).

According to Herndon et al (1999), few attempts were made to regulate water pollution in USA until introduction of the Federal Water Pollution Control Act of 1956 and the Water Quality Act of 1965. However, the establishment of the Environmental Protection Agency in 1970 marked the beginning of an aggressive federal effort to improve the quality of American waterways. The US Congress passed the "Pollution Prevention Act" in 1990 to encourage industries to reduce pollution (US EPA, Pollution Prevention Research Plan, 1990). The concept of zero discharge had become a principal focus of industrial wastewater treatment. Industries started to view wastewater treatment as a cost of doing business. Due to growing environmental awareness in society, stricter environmental regulations and the realization in industry that reuse and recovery of water improves the financial bottom line, industries are now compelled to implement the reuse/recycle option.

Linhoff and Smith (1994) noted that industries pay for wastewater treatment by volume, and the cost of wastewater treatment nearly always exceeds the cost of raw water. It is easy to see therefore how conserving water can lead to savings by reducing treatment costs. Environmental laws that regulate the impact of industrial discharges have also motivated industries to minimize the amount of effluent that leaves their plants. Typically some type of effluent reuse or recycling is introduced in an effort to minimize or even eliminate wastewater discharge. Examples of these types of water conservation methods can be found practically in every industrial sector (Ross and Sasser, 1998).

According to Herndon, et al. (1999), much good has come out of the drive for industrial wastewater treatment during the past 30 years. New technologies have been developed, older technologies have been improved and companies have realised their responsibility for environmental preservation. Thus the future of industrial water conservation lies in the ability of the scientific and engineering community to develop new technologies for optimising the use of available water. After all, creation of new sources of water, for example by way of desalination plants, is cost prohibitive., For example, the cost of desalinated water production in Kuwait is about 10 US$/1000 IG. In addition to the high cost of produced water, the energy required for producing such water is derived by burning fuel, which adds to the environment pollution. Hence, it is only through conservation methods such as more efficient means of reuse, recycling and alternative use that future water requirements can be met. Such conservation methods include approaches such as process changes, equipment types or operational procedures that make it possible to use less water (Ross and Sasser, 1998).

Currently most wastewater is released to the sea, river, lake, etc. However, in many cases it is feasible for treated wastewater to be reused because certain uses do not require high quality water. If wastewater is reused then the total water demand and the effluent treatment load can be lowered (Nobel and Allen, 2000).

The objective of waste minimization strategies in the process industries should make waste management more sustainable by moving up the hierarchy of options. The hierarchy shows that the first priority of any industry is to avoid producing wastes in the first place; if it must be produced, then the quantity should be minimized. The next step is to re-use or recycle as much as practicable. Treatment should then be aimed at recovery of energy and at minimization of the quantities requiring final disposal. Only then, should the residues be considered for disposal. Current pollution prevention practices in process industries should be aimed at the top of the cone as indicated in Figure 2.1 which depicts the general waste management hierarchy (Wilson, 1996).

Douglas (1992) stated that the general perceptions and experiences in the area of reuse and recovery of process water are that it is a non-core business cost or a necessary evil to satisfy demands from environmental and public pressure groups. Nonetheless, even though the initial capital outlay may introduce a financial strain, in the long term the benefit should significantly outweigh the drawbacks.

Reduction of polluted wastewater can be achieved by process redesign with integrated technology. However, the technology for improving a process by avoiding or reducing residues is not always available. Each process must be researched and developed separately. This requires both time and money. A new production process with integrated technology can be implemented only if its costs are lower than the sum of the costs of the old technology and the end of pipe treatment. The polluted wastewater that unavoidably occurs (even under optimum operating conditions) can be partially reused/recycled after proper treatment. However, the recovery of residues from wastewater and their reuse in plant may also be limited for technical reasons. It is only after such measures have been adopted that end of pipe technology comes into play. End of pipe measures however constitute unproductive capital (Christ, 1999).

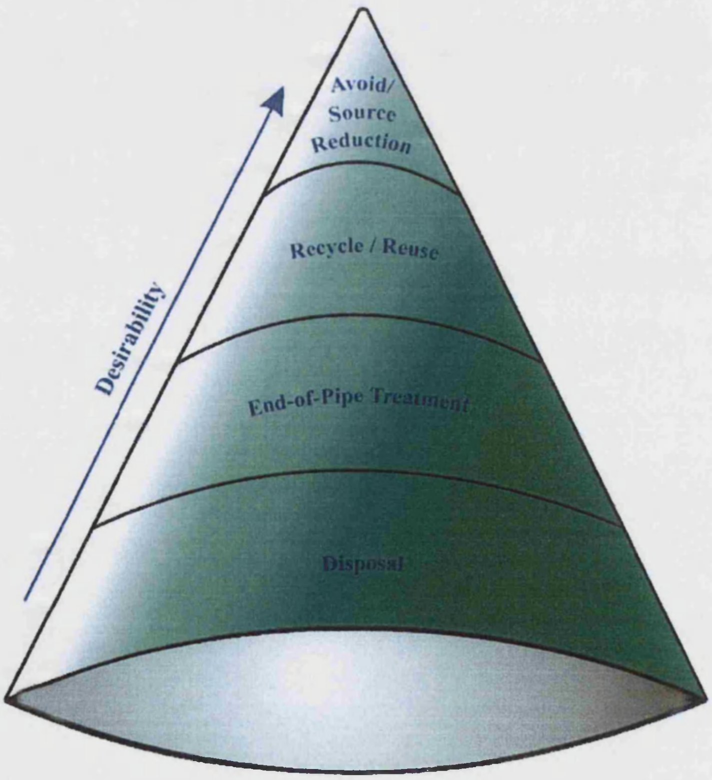


Figure 2.1: Waste Management Hierarchy (Wilson, 1996)

The waste management hierarchy is also addressed by Smith (1995). It defines the following four general approaches to wastewater minimization:

a) Process changes. These are made to reduce the demand for water. For example, use an air cooler instead of a cooling tower. Process conditions are changed to reduce pollutant concentrations.

b) Water reuse. Wastewater generated from one unit can be reused in another process unit, provided the used water quality meets the necessary requirements of the second unit.

c) Water regeneration and reuse. Wastewater generated from one unit, and processed in another unit to reduce the contaminant level, is reused in another unit.

d) Water regeneration and recycle. Waste water generated from one unit, and processed in another unit to reduce the contaminant level, is recycled back to the same unit.

The following checklist provides some options for process changes that can be considered to reduce wastewater generation in a typical industry (Rossiter et al., 1993 and Nelson, 1999):

1. Is it possible to improve the feed quality?
2. Can any input stream be eliminated?
3. Can any waste stream be used in the process?
4. Should impurities be removed before processing?
5. Is it possible to reduce the off-specification?
6. Is it possible to optimize the product quality?
7. Can inhibitors be used?
8. Can a better feed distributor in the unit/reactor be obtained?
9. Is it possible to improve the catalyst?
10. Is it possible to introduce heat integration?
11. Does advanced process control help?
12. Is it possible to monitor and reduce fouling by online cleaning

13. Should the reflux be optimized?
14. Does reducing the pressure improve separation efficiency?
15. Is it possible to eliminate leaks?
16. Can waste by product be recycled to extinction?
17. Can waste be reduced by addition/modification of unit operation?

Most water reuse/recycling programmes are carried out within a single company site. However, extensive work on the possibility of reusing treated wastewater amongst industries located within a geographical region has been made. It is believed that this type of integrated water reuse management provides economies of scale and more reuse opportunities. However, planning and designing water reuse programme at a regional level require data gathering on the quality of available wastewater and the geographical location of the industries where the supplies and demands occur (Nobel and Allen 2000). This concept of coupling reuse analysis with geographical information systems is not limited to water reuse alone.

A checklist that helps in identifying the wastewater generation in a typical refinery, and the steps required to reduce it, are given below. The objective in this case is selection of suitable methods to reduce the generation of waste and increase recycles (Klee and Podar, 1991).

i) Replacing steam ejectors with vacuum pumps will reduce sour water generation and steam use.

ii) Two-stage desalting will reduce brine flow and oil loss.

iii) Replacing live steam with reboilers in crude distillation units will reduce sour water generation.

iv) Using stripped sour water for line washing will reduce the water import.

v) Using stripped sour water for the generation of stripping steam.

According to Doran and Williams (1999), the basic message in the analysis of any process is: "don't solve an end of pipe problem with an end of pipe solution unless you have explored all process solutions; your end of pipe solutions could be the worst solution to your problem".

According to Crittenden (2001), treatment and disposal are the final waste management options which should only be used once other avenues of prevention, minimization and recycling have been exhausted. All wastes and discharges must be treated in order to render them harmless. This is the lowest level in the hierarchy and does not merit the labels of clean technology.

2.4. Benefits of Waste Minimization

Actual experiences in pollution prevention and waste reduction in the process industries have been reported extensively in the literature. The main benefits and difficulties encountered in implementing such practices have been highlighted. Dantus and High (1996) reviewed the benefits achieved by a number of organizations by implementing waste minimization programs. The reported examples are summarised as follows:

a) As part of their Waste Minimization Program, between 1983 and 1988, *Amoco* reduced its hazardous waste by 86%, saving the company about $50 million.

b) Between 1987 and 1990, *Chevron*, under its "Save Money and Reduce Toxics Programme (SMART, 1987)" program, reduced hazardous waste by 60% and saved more than $10 million in disposal costs.

c) *Dow* reported that it had achieved a 31% reduction in its overall releases between 1987 and 1989 as part of its Waste Reduction Always Pays (WRAP. 1986) program. It had also reported an over all reduction of 15% in air emissions for 1989, and a 54% decrease from 1984.

d) *General Dynamics* under its "Zero Discharge (1985)" program eliminated nearly 40 million pounds of hazardous waste discharge from 1984 to 1988 (approximately 72%), even though sales and production increased from $7.3 to 9.35 billion over the same period.

e) Hazardous waste generation in *IBM* was reduced by 38% between 1984 and 1988 84% of IBM's hazardous waste was recycled in 1988; 28% of all solid waste from

IBM U.S. operations was recycled in 1986. IBM U.S. emissions were reduced by 20% from 1987 to 1988 and IBM U.S. had a decrease of 25% in its CFC (Chlorinated Fluoro Carbon) emissions between 1987 and 1988.

f) A demonstration project on wastewater minimization was completed in 1995 in the *Aire and Calder* catchments of West Yorkshire (UK). Edwards (1996) reported that the findings indicated cost savings of over £3 million /annum for eleven firms. The reduction in the amount of wastewater discharged either to sewer or river was 27% with a potential further 10%. The payback period for over 63% of opportunities was less than a year.

Besides the above, other literature sources also reveal significant reduction in waste generation and they are summarized below:

i) Zbontar and Galvic (2000) presented an analysis of wastewater streams in a refinery and petrochemical complex. They identified sources for possible reductions in flows of wastewater using wastewater reuse or preliminary regeneration and reuse. The consumption of fresh water could be lowered resulting in annual savings of US$ 27,630 with a payback period of 6 months in the petrochemical plant and US$15,500 with a payback period of 11 days in the refinery.

ii) In 1993, the US Department of Energy formed Industrial Assessment Centres (IAC) to assist small and medium sized manufacturers to improve their energy efficiency and analyse their waste streams. Kirsch and Muller (1996) reported that the average annual waste saving per client served by the IAC programme was US $20,000 in the 1994 fiscal year. These savings were created with less than a three-year return on investment.

iii) Benforado and Ridlehoover (1991) studied waste reduction in amine production units. They indicated that by increasing the conversion, wastes could be reduced by 95 tonnes/yr. Moreover, by considering the recycling of excess reactants, an additional waste reduction of 70 tonnes/yr and a decrease of 20% in manufacturing costs could be obtained.

iv) Wang and Smith (1994) presented a case study of minimization of wastewater in a petroleum refinery. Through re-use, fresh water consumption, wastewater generation and total cost was reduced by 20%. Adding regeneration processes without recycle reduced fresh water and wastewater flow rates by nearly 60% and reduced cost by more than 60%.

v) Suriyaprapadilok (1998) formulated non linear programming (NLP) to solve the optimum water using network problem in a tapioca plant and reduced freshwater consumption by 13%.

vi) Another waste reduction exercise in an amine production process was carried out by El-Halwagi and Spriggs (1995). They proposed the use of a mixed integer non-linear programming (MINLP) model for the synthesis of mass exchange networks for purification.

vii) Bonom et al. (1999) indicated that the interest in wastewater reuse in Italy began to grow during the 1980s when a sufficient flow of treated wastewater from wastewater treatment plants became available and reclamation programme for agricultural and industrial purposes began to be taken into account. They commented that from 1990, specific water consumption per unit production dropped from 40 to 6 m3/tonne in the recycled paper industry, and by 20% in tanneries. They also indicated that part of the treated effluent water could be filtered, polished and used in cooling towers.

viii) Because of an increasing water shortage in Belgium, Terras, et al. (1999) commented that it was necessary to switch over to alternative industrial water supply sources. They concluded that advanced water purification treatment in combination with process control has helped to reuse part of the effluent water in a jeans finishing plant.

Mulholland and Dyer (2001) claimed that *Dupont* is a pioneer in introducing pollution prevention by waste management. They reported that Dupont had developed a methodology that identified the technologies and practices to reduce waste generation. The methodology examines the process, starting with the waste streams and working backwards to their source, asking questions about how to eliminate or minimize the waste at each step. The following four steps are used to arrive at the best option:

1. List all components in the waste stream along with key components.

2. Identify the component that causes the problem; then develop a waste minimization option to reduce/eliminate the generation of the component.
3. Identify the highest volume materials because they control the operating costs associated with treatment of wastes.
4. Develop a waste minimization option to reduce the volume.

Doran and Williams (1999) carried out a pilot plant study to convert unusable oil-field produced water into a drinking water resource. Results from a 10 gallons per minute (gpm) pilot plant was used for conceptual design and cost estimation for a 44,000 barrel per day (bpd) treatment facility to treat oil-field produced water to meet California potable water standards.

The wastewater reuse project at *Esso Nederland*, Rotterdam refinery proposed to treat the effluent from the wastewater treatment plant and reuse it as fresh water make up, instead of draining it off into the harbour. Duyvesteijn (1998) reported that the reuse of the wastewater treatment plant effluent is limited by the presence of suspended solids and the relative high conductivity. It is shown that it is technically feasible to upgrade the wastewater treatment plant so its product could be reused as demineralization plant feed. The reuse project is made use of 200 m^3/hr reverse osmosis permeates.

In short, there are many opportunities for industrial manufacturers to reduce waste costs in their facilities. To accomplish this, they must examine their waste streams and monitor them closely. Then they can reduce costs through process changes, implementing new technologies or selling waste products to recyclers (Wilson, 1996).

2.5. Wastewater Minimization Techniques

In order to reduce pollution and improve wastewater minimization, different types of technology have evolved simultaneously. They differ widely in scope and approach. However, the ultimate aim for these technologies remains pollution prevention and waste reduction. Depending upon the nature, type and size of process units, different methods are selected for a given situation to reduce the cost and time required in developing the model.

Given a set of water using/water disposing processes, it is desired to determine a network of interconnections of water streams among the processes so that the overall fresh water consumption is minimized, whilst the processes receive water of adequate quality. This is referred to as the water/wastewater allocation planning (WAP) problem as detailed by Bagajewicz and Savelski (2002).

The oil and gas industry, along with a range of other production industries, is interested in dealing with waste management problems in a proactive manner. A waste reduction model has to be developed to assist in the long term planning of waste reduction and waste management strategies. In their technical notes Roberge et al. (1994) commented that when developing the model, emphasis should be placed upon development and expansion of on site waste management facilities and interaction between these treatment/disposal facilities and production units with waste reduction potential. This modelling approach could also be used in the short to intermediate term for the investigation of waste reduction options with no, or low, capital cost requirements to reflect the realities of industrial waste management in difficult economic conditions. This approach will minimize the overall cost of waste reduction and waste management for an industrial facility over a defined time period where a combination of many potential options can be considered. The model can be used as an aid in an overall decision-making framework.

The waste reduction optimization modelling approach is potentially useful for the evaluation of waste reduction alternatives and for implementing a structured approach to waste management planning. The process of developing the required information and applying a systematic approach allows for questioning the current waste management practices and methods, as well as the identification of areas where information and knowledge is lacking. The modelling approach is most useful when the information used in developing the mathematical formulation is as reliable and accurate as possible and when the problem being studied has a significant degree of complexity (Roberge et al., 1994).

The first step in a waste minimization programme is to identify where waste is generated and how much it is costing (Maunder, 1999). According to Fromm et al. (1987), the approach should start with compiling all waste streams leaving the plant. The available plant piping and instrumentation diagrams (P&IDs) and a site visit (including a guided tour of facilities) should provide all the required information about the plant. Waste streams should be quantified on a uniform basis. Once all the streams have been identified, then each stream should be expressed as a percentage of the total quantity of waste leaving the plant. Then a waste tracking model is developed in the form of a flow diagram, which identifies the cost of wasted resources during each step of a particular process. Armed with this information, the waste stream that is to be immediately targeted can be identified. Fromm et al. (1987) listed the following criteria which should be used while deciding on the targets:

1. Method and cost of disposal
2. Composition of waste
3. Quantity (present and future)
4. Degree of hazard (toxicity, flammability etc)
5. Potential for minimization
6. Compliance status (present and future)

Thus, the model looks at how process waste is created and how it can be reduced or avoided. Once potential sources of savings have been identified using the waste tracking model, then it is easy to tackle the problems one by one (Maunder, 1999).

Many methods are available to study the reduction in wastewater production. These are basically integration techniques for both new and retrofit applications. The techniques can be mathematical, thermodynamic and economic based models, and can include, artificial intelligence (AI), hierarchical analysis, pinch analysis and mathematical programming. They vary significantly in their scope and approach.

There is a significant overlap between the various methods and today's trend is strongly towards methods that use all the mentioned above. The large number of structural alternatives in process design (and integration) is significantly reduced by the use of insight, heuristics and thermodynamics and makes it feasible to address the remaining problem of multiple economic trade-offs using optimization techniques (Gunderson, 2002).

Pinch technology and exergy analysis are methods with a particular focus on thermodynamics. Hierarchical analysis and the use of knowledge based systems are rule-based approaches with the ability to handle qualitative (or fuzzy) knowledge. Optimization techniques can be divided into deterministic (mathematical programming) and non-deterministic methods which are also called simulated annealing and genetic algorithms (Gunderson, 2002).

2.5.1. Pinch Technique

Linhoff and Smith (1994) noted that industries pay for wastewater treatment by volume, and the cost of wastewater treatment nearly always exceeds the cost of raw water. They developed pinch technology that was originally designed for heat transfer applications and which was mainly applied to recover heat from process units through process integration. Pinch analysis can reduce energy consumption and at the same time establish targets for optimum energy consumption, design heat integration systems for optimum heat recovery, and optimize utility systems (steam, cogeneration, refrigeration, furnaces, etc.).

Applications of pinch technology include both new plant designs and retrofits of old plants. Pinch technology has been successfully used in improving energy efficiency, optimizing utility systems, reducing emissions, reducing capital costs, and de-bottlenecking process units.

Pinch analysis has the following advantages over "conventional" design approaches:

i. A systematic procedure. It guarantees an optimum solution without relying on luck or inspired guesses by the design engineer.

ii. A common denominator methodology. Based on fundamental thermodynamics, pinch analysis applies to all processes and technologies, continuous and batch, new and retrofit.

iii. Proven energy savings. Reductions of 15% or more in energy cost are typical, even where processes have already been optimized by "conventional" methods.

iv. Automatic pollution prevention. Reduced CO_2, SO_x and NO_x emissions are the natural consequence of better energy efficiency.

v. Lower cost de-bottlenecking. Pinch analysis shows how to make better use of existing equipment and systems, and thus minimizes new equipment requirements in capacity of units.

Even though pinch technology had been developed for heat transfer applications, it can be effectively used for mass transfer applications including water pinch and hydrogen pinch El-Halwagi and Spriggs (1995). Tainsh and Rudman (1999) explained that water pinch is the systematic technique for analysing water networks and reducing the water cost for process. It uses the advance algorithm to identify and optimize better water reuse, regeneration, and effluent treatment opportunities. Generally, the water minimization and wastewater design are done independently even though they are closely interrelated. Kuo and Smith (1998) explored the design options to solve the problems simultaneously.

Detchasit and Thongchai (2004) used MATLAB™ to simplify pinch technology using generic algorithms. This technique is useful for simple problems using a single component contaminant. It is difficult to handle multi component contaminants using their technique.

2.5.2. Mathematical Programming

The name refers to a sub-class of methods from Operations Research. The salient features of the method are as follows

- it is based on the use of Mathematical Models
- it can handle both discrete and continuous variables
- it provides simultaneous optimization of process structure and parameters
- it provides targets for heat exchanger / process networks (exergy by an LP model)
- number of units are evaluated by Mixed Integer Linear Program (MILP) model and area by Non Linear Program (NLP) model.
- possible framework for automatic design.

- proper optimization of multiple Trade-offs due to its simultaneous nature.

El-Halwagi and Spriggs (1995) indicated that mass integration provides a comprehensive methodology for targeting yield, emissions, capacities, design reactions, separation and waste processing systems. It is now playing an important role industrially. This method can be successfully applied to meet environmental and other regulations to reduce gaseous emissions, water use, wastewater treatment and waste disposal.

Doyle and Smith (1997) considered two cases in targeting maximum water reuse. The optimization problems were formulated as a nonlinear problem for the fixed mass load assumption, and a linear problem for the fixed outlet concentration assumption. The authors combined the proposed mathematical method with a graphical representation which incorporates various types of constraints. Outlet concentration is a function of process parameters, however most mathematical models available in literature have attempted the water reuse problem by assuming that water always removes fixed loads of contaminants. Another assumption is that solubility and corrosion limits can be used to set maximum inlet and outlet concentration units imposed on contaminants. These assumptions are necessary to simplify the problem and make it easier to solve (Bagajewicz, 2000).

Bagajewicz et al., (2000) presented a simple new approach for the grassroots and retrofit design of water utilization systems with multiple contaminants. The method describes maximum reuse while minimizing not only fresh water make-up but also cost. One important conclusion of this paper is that for real systems, the problem can exhibit several sub optimal alternative solutions that are very close in cost to the optimal one.
Bagajewicz et al., (2001) further developed this technology by combining mass and energy transfer together and solving the problem simultaneously. This methodology has taken into consideration the simultaneous interaction between water optimization and heat minimization.

NLP is further enhanced by Wang et al (2002) by introducing a new concept of the internal water main, which is related to the maximum water-saving potential. However, this might have an impact on the unplanned shutdown of some units and so affect the overall water balance.

Bagajewicz and Savelski (2003) have presented the necessary conditions of optimality for multicomponent water allocation systems in refineries and process plants. It is shown that at least one component reaches the maximum concentration at the outlet of a freshwater user process. Monotonicity conditions have also been derived.

2.5.3. Mass Exchange Networks

A mass exchange network has been defined as (El-Halwagi, 1997): "a system of separators and mass transfer units that achieves in a cost effective manner minimal discharge of hazardous streams". The purification of the waste streams can be accomplished using existing streams in a process or utility using mass separating agents (MSA), which define the operating cost of such a venture (Hallale and Frase, 2000).

Alva-Argaez et al., (1999) combined insights from water pinch with mathematical programming. Their approach applies to mass exchange network and wastewater minimization problems and the purpose was the development of targeting models at a conceptual stage where the process network is not yet developed. However for wastewater minimization, this concept of limiting water profile is employed.

A Mixed Integer Non-linear Programming (MINLP) model was proposed by Papalexandri et al. (1994) for the synthesis of mass exchanger networks for the purification of process streams, via the use of MSA. Mass integration is driven from the minimization of a total annualised cost. The model is based on a hyper-structure representation of all the alternatives for the available rich (high concentration) and lean (low concentration) streams (splitting, recycling, and regeneration). Both operating cost and capital cost are optimized simultaneously. The solution of the resulting MINLP model provides a mass exchanger network which satisfies the specifications on target compositions (environmental or process requirements) at minimum total annualized cost. Cohen and Allen (1992) describe the same.

2.5.4. Hierarchical Analysis

This is one of the oldest methods used for pollution prevention. Creative engineers have historically accomplished the development of process improvements to reduce emissions on an adhoc basis. Over the past 20 years many worthwhile advances have been made in this way. Douglas (1992) developed a systematic approach to process design by reducing the design problem to a hierarchy of decisions. The hierarchy of decisions is:

i. Batch versus continuous

ii. Input-output structure of the flowsheet

iii. Recycle structure of the flowsheet

iv. General structure of the separation system

    a. Vapour recovery system

    b. Liquid recovery system

v. Heat-exchanger network

The hierarchical method also provides a framework for identifying process improvement options by evaluating heat and mass integration opportunities (Rossiter and Spriggs, 1993). The main characteristics of this method are based on:

1. the idea of a decision hierarchy
2. extensive use of heuristics and partial cost estimates
3. interactive approach (engineer in control)
4. traditional design practice put into a systematic methodology

Forstmier et al., (2004) used this approach in a liquid detergent plant to optimize the water network. The design hierarchy was further studied and explored by a number of researchers (Banares-Alcantara and Lababidi, 1995). An initial hierarchical decision procedure which provides a systematic method for identifying process modifications to minimize waste generation was developed by Smith and Petela (1991). They developed an 'onion' diagram of four layers. The inner layer is the reaction section followed by the separation and recycle system, then the heat exchanger network followed by the utilities system. The proposed diagram stimulates design engineers to think about two distinct classes of waste which might arise from a chemical process: process waste and utility waste. The process waste is generated from the reaction and separation systems (two inner layers), while the source of the utility waste is from the heat exchangers and utility systems. Process waste consists of unwanted by-products and purge streams, while utility waste comprises the products of fuel combustion, waste from boiler feed water treatment as well as from boiler and cooling tower blow downs.

The 'onion' diagram was adapted by Crittenden (2001). The diagram was modified to include the provision of products and services as shown in Figure 2.2. The argument here is that the provision of a service should be at the heart of the diagram because to provide a service, a product should be manufactured. A number of steps are required to manufacture the product, and each step would consume resources and energy and lead to process and utility wastes. Moreover, the product itself might eventually become a waste.

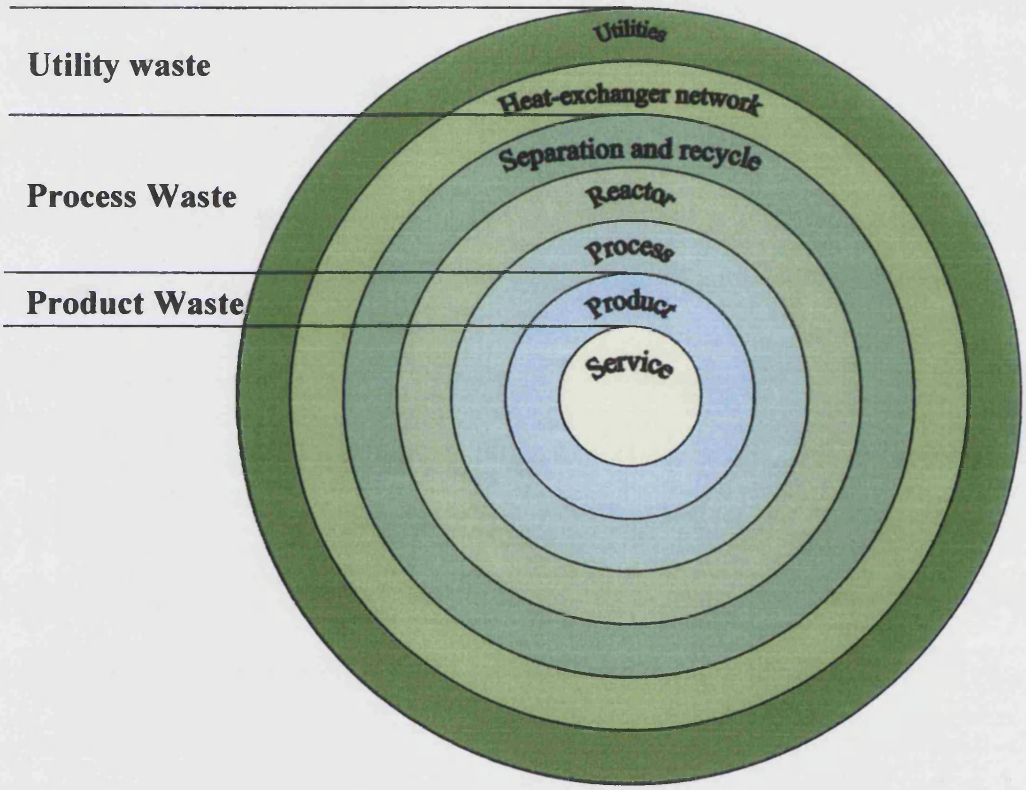


Figure 2.2: Modified 'onion' diagram for waste minimization. (Crittenden, 2001)

Clift (1995) stated that the hierarchical approach has been used in the design of various types of plant and has been adapted for retrofit applications. For example, this procedure was successfully applied to the crude unit, FCC unit and sour water system at AMOCO's Yorktown Refinery.

2.5.5. Artificial Intelligence

One of the most effective means of minimising the generation of wastes in the process industry is through process design/modification and process control. It is very difficult to resort to conventional algorithmic methods to design and control a process with waste minimization in mind when the available information pertaining to a process is imprecise, incomplete, uncertain and the accessible knowledge is in symbolic form. Artificial intelligence (AI) techniques are viable alternatives for dealing with information and knowledge of this type. Huang and Fan (1993) have amply demonstrated this successfully by developing three intelligent systems for waste minimization. It is conceivable that AI techniques will play an increasingly important role in waste minimization in the future. An AI paradigm that proved promising in waste minimization applications is the knowledge-based system or expert system. It is difficult to incorporate this type of design (for a refinery water network) through AI since many uncertainties are involved and many cases have to be developed to formulate the AI model. Considering the complexities to develop such a model, AI is not considered in this thesis.

2.6. Process Integration

Starting in the 1970s, engineers began to realise that correctly assembling the process building blocks is just as important as properly selecting and designing individual components. They also discovered that fundamental principles could guide this assembly. This led to the concept of integrated process design or process integration, which emphasises the unity of the entire process. It addresses the overall system first using fundamental principles and it then tackles the design approach at different levels (El-Halwagi and Spriggs, 1995).

Basically, the waste reduction model uses an optimization technique to determine an overall strategy for minimising the cost of waste reduction treatment and disposal options. The different options and their associated costs as well as other economic and technical information, are required as input data. The program can be run on a microcomputer using a commercial software package. In this the objective function represents the capital and operating costs of the existing and proposed waste reduction and waste management options. The constraints represent the limitations (Roberge et al., 1994).

Process integration can be applied to a typical oil refinery which is a main industrial water consumer. Refinery facilities consist of sophisticated networks of process units, which are generally integrated to reduce the processing cost. These units interact with each other depending on unit operations and the final economic requirement of the product slate. Methods used for this type of problem should be capable of handling many units. The method should also have provision to apply regeneration/ recycle/ reuse options to reduce the wastewater generated. Huang, et. al. (1999) applied mathematical modelling to a Japanese refinery and reduced fresh water consumption from 765 tonnes/hr to 591 tonnes/hr.

2.7. Uncertainties

Due to economical and logistical reasons, many units can operate at different capacity and severity levels. This often leads to uncertainty in waste production and processing. For example, wastewater is produced from many units and each stream has a different contaminant level. Mixing of these streams might make an entire stream unfit for reuse/recycle. The nature of the impurities in some streams will make it possible for recycle or otherwise reuse. For instance, sour water from a vacuum distillation unit (VDU) has only around 89 ppm H_2S compared to the atmospheric desulfurization unit with 41,660 ppm. In such a case integration becomes more difficult. Generally, the worst cases are considered for design but often lead to over sizing of equipment at higher cost.

Bagajewicz (2000) indicated that wastewater flow as well as contaminant level can vary widely for refineries and thus the proposed design should be resilient to accommodate the variations. The best way to solve these types of problem is by using stochastic programming, which is essentially tailor - made to handle uncertainties.

For many systems, the concentrations of contaminants may reach their solubility limits, but such limits are functions of process parameters (temperature and pressure). Hence the loads of contaminants are variable with respect to the flow rate (Huang et al., 1999). This suggests that the design of wastewater networks should be resilient and able to accommodate different pollutant levels (Bagajewicz, 2000) which may easily result from deviations in operating conditions.

The impact of uncertainties on optimal wastewater networks has not been studied, except by Linniger et al. (2000). They studied waste reduction in a batch process for pharmaceutical production using an uncertainty model, which was incorporated essentially to facilitate decision making for the solvent recovery and treatment process. However, there is a rich literature in studying the effects of uncertain parameters on the resiliency of heat exchanger networks (Floudas and Ciric, 1989; Galli and Cerda, 1991; Hu et al., 1993; Aguilera and Nasini, 1995). Recently, a number of researchers have reinitiated the area of "process design under uncertainty". Cheng et al. (2003) provided a brief review of this subject and formulated design and planning under uncertainty as a multi-objective decision process

Many papers are being published in the area of designing and planning new process units under multiple kinds of uncertainties such as market conditions, product quality and technological evaluation. This allows decision-makers to provide multiple criteria – such as expected profit, expected downside risk, and process lifetime – that reflect various conflicting or incommensurable goals. This integrates design decisions and future planning by constructing a multi-period decision process in which one makes decisions sequentially at each period. The decision process explicitly incorporates both the upper-level investment decisions and the lower-level production decisions as a two-stage optimization problem (Cheng et. al., 2003).

Until now, no literature is available on uncertainties in wastewater qualities of a continuous process industry such as an oil refinery

2.8. Sustainable Production

Sustainable development is the management and conservation of the natural resource base and the orientation of technological and institutional change, in such a manner as to ensure the attainment and continued satisfaction of human needs for the present and future generations (Zadorsky, 1999).

The main theme of the European Round Table on Cleaner Production (1998) stated that cleaner production is a strategy to continuously improve eco-efficiency by minimising environmental impacts in all societal activities, throughout the entire life cycle of the products, minimizing the quantity and toxicity of all waste at source, minimizing the use of hazardous raw material and process, non renewal resources, water and energy.

Any product or process has continuous interaction with the environment from the design stage to the de-commissioning stage (or beginning to end of life of the product). Clean technology is a means of providing a human benefit which overall uses less resources and causes less environmental damage than alternative means with which it is economically competitive (Clift, 1995).

Klee and Podar (1991) of BP Amoco indicated that the need to create a suitable company that will protect the environment and improve quality of life as a responsible corporate citizen. Thus by reducing wastes, either at source or by recycling / reusing, the depletion of natural resources are protected and preserved for future generations.

Life cycle assessment (LCA) is a widely accepted methodology that enables quantification of environmental impacts and evaluation of the improvements throughout the life cycle of a process/ product. An LCA study begins with decisions on the goals of the study and this helps to set the boundaries - those parts of the life cycle inside the boundary must be included. Other parts, judged to be insignificant, may be omitted (Mata and Costa, 2000).

LCA users attempt to trace back to the environment all of the resources consumed at all stages in the manufacture, use and disposal of products. In addition, all of the emissions to air, water and land at each of these stages are also accounted for. These data form a life cycle inventory of exchanges of substances between the product and the environment associated with the entire life cycle of the product, from the 'cradle to the grave' (Mata and Costa, 2000).

At the impact assessment stage of an LCA, the potential contributions made by each of the environmental exchanges to important environmental effects such as global warming, acidification, photochemical smog, human- and eco-toxicity, eutrophication and the depletion of non-renewable fossil fuel resources, is calculated. The results of the assessment are then interpreted, in the light of local, national and international pressures, for their level of relative significance. The original goals of the study are addressed, as are the consequences associated with alternative raw materials, processes and products. It is often possible to make recommendations for targeting the most significant environmental impacts and those parts of the life cycle, which contribute most to the impacts (Mata and Costa, 2000).

Based on the recommendations, the plant/process should be suitably modified. The design and retrofits of process are creative activities, whereby new ideas are generated which are then translated into equipment and process for producing new material or upgrading the value of existing materials or process (Mata and Costa, 2000). During retrofits more care should be taken to integrate the new facilities with existing facilities, with minimum environmental impact so as to have a favourable rating during LCA.

2.9. Conclusion

Process synthesis and process integration have continuous variables like temperature, flow rate, pressure, etc and discrete variables like selection of equipment, location, sequencing, etc. These continuous and discrete variables which are constrained optimization problems, can be accommodated easily in mathematical programming.

Problems related to mathematical programming such as local optima caused by no convexities in the models, discontinuities and combinatorial explosion can be overcome by using Simulated Annealing and Genetic Algorithms in Process Integration. (Dolan et al., 1989, and Nielsen et al , 1997). Apparently, there has been less use of Genetic Algorithms in Process Integration, but one application has been described by Lewin, 1998a,b.

Basic concepts in pinch analysis, which was originally developed for heat integration, are the composite curves which give the engineer an overall view of the opportunities for heat recovery in the total process, in a single diagram. However applying such techniques for waste water minimization will not be appropriate as it is difficult to properly address the multiple trade-offs involved, due to the sequential nature of pinch methods. If low contaminant streams are excluded, as followed in pinch analysis (for reasons such as safety, operability, piping difficulties, contamination prevention, etc.), it becomes extremely difficult to maximize water reuse. The pinch design method is also quite time-consuming, and even though the matching rules are simple, it often requires major effort to develop a valid initial design.

In summary, there are limitations in many phases of pinch analysis, such as the problem definition phase (hard to handle forbidden matches), the targeting phase (approximations and heuristic rules that fail), as well as the design and optimization phase (multiple tradeoffs, topology traps, etc.). Mathematical programming overcomes all these limitations and such situations can be formulated and solved easily.

Finally, it should be noted that Mathematical Programming provides a framework for automatic design, which means that time (which is a limiting factor in many engineering projects) can be saved and used for more high level decisions.

Chapter Three

3. NONLINEAR AND STOCHASTIC PROGRAMMING

3.1. Introduction

In an optimization problem, one tries to minimize or maximize a global characteristic of a decision process such as elapsed time or cost, by exploiting certain available degrees of freedom under a set of restrictions, termed as constraints. While the word optimization, in non-technical language, is often used in the sense of improvement, the mathematical optimization community adheres to the original meaning of the word related to finding the best solution either globally or at least in a local neighbourhood (Kallrath, 2000).

A mathematical model in optimization theory consists of four key components:

1) **Data:** also called the constants of a model. These may represent limiting concentrations, flow rates, operating conditions, targets and so on.

2) **Variables:** also called decision variables or parameters, and may be continuous, semi-continuous or binary integers. The variables represent the degrees of freedom that are necessary to make a decision. Examples include the freshwater demand, amount of water recycled or reused, and amount of regenerated water.

3) **Constraints:** also called as restrictions, and include equality and inequality equations. Constraints can be a wide range of mathematical relationships (algebraic, analytical, differential or integral) representing mass balances, quality relations, capacity limits, and so on.

4) **Objective function:** expresses the goal to maximize or minimize. Examples include minimizing freshwater flow rate, wastewater disposal and operating costs, or maximizing recycle and reuse and utilization rate.

Mathematical models for optimization usually lead to structured problems, which are classified based on the linearity and types of the variables (real, binary or integer) and constraints. Common optimization problems include:

a. Linear Programming (LP) problems.

b. Mixed Integer Linear Programming (MIP) problems.

c. Nonlinear Programming (NLP) problems.

d. Mixed Integer Nonlinear Programming (MINLP) problems.

A model in which the objective function and all of the constraints (other than integer constraints) are linear functions of the decision variables is called a *linear programming* (LP) problem. If the objective function, or any of the constraints, is not a linear function of the decision variables, the model is called a *nonlinear programming* (NLP) problem. If the problem includes integer constraints, it is called an *integer linear* or *integer nonlinear* programming problem, respectively. A linear programming problem with some "regular" (continuous) decision variables, and some variables which are constrained to integer values, is called a *mixed-integer programming* (MIP) problem.

A *quadratic programming* (QP) problem can be thought of as a generalization of a linear programming problem, or as a restricted case of a nonlinear problem. Its objective is a quadratic function of the decision variables, and all of its constraints must be *linear* functions of the variables. A QP problem is a special case of an NLP problem.

Besides building a model and classifying the problem, a solver is needed to solve the problems listed above. A solver is software consisting of a set of algorithms for solving optimization problems.

Optimization problems arise in almost all branches of the chemical process industry. These include product and process design, production, logistics and even strategic planning. Most recently, experiences in optimizing such traditional problems have been heavily utilized in optimizing water networks.

Kallrath (2000) listed some areas in which applications of linear and nonlinear mixed integer optimization are found in the process industries. These include: production planning (production, logistics, marketing), sequencing problems (putting production into order), scheduling problems (production of goods requiring machines and/or other resources), allocation problems (allocating resources to orders and people to tasks), blending problems (production and logistics), refinery planning and scheduling (refineries and chemical process industry), process design (chemical process industry, food industry and refineries), selection and warehouse/depot location problems (strategic planning), investment and de-investment design problems (strategic planning), network design (planning and strategic planning) and financial problems (strategic planning).

The current work involves developing two types of mathematical model, namely, a *deterministic model* and a *stochastic model.* Mathematical deterministic models are used for problems in which the variables are known and specified. The most commonly used mathematical programming technique is linear programming (LP). This method works only if all the constraints and a single objective function can be expressed as linear equations. LP assumes that the decision variables can be expressed as continuous variables.

If some decision variables can only be expressed as integer variables, LP does not work. For example, if the decision is to incur a production changeover or setup, this can be expressed as a *zero-one* variable. To handle this, mixed integer programming (MIP) should be used. In contrast to LP, however, while an optimum solution can be generated, it may take a considerably longer time to solve. Other mathematical programming methods include nonlinear programming and dynamic programming.

Decision makers often have to make decisions in the presence of uncertainty. In this case, decision makers wish to solve optimization problems which depend on parameters that are unknown or difficult to forecast. The stochastic optimization approach is one of the most often used approaches to decision making under uncertainty.

The deterministic model for optimizing wastewater networks is nonlinear in nature. The nonlinearity mainly arises from multiplying the water flow rate with the concentration of the contaminants.

This chapter is devoted to providing the necessary background about the optimization methods used in the current work. The following sections introduce nonlinear programming and stochastic programming. The last section gives a brief overview on GAMS, the optimization solver used in solving the proposed optimization models.

3.2. Nonlinear Programming

A nonlinear programming problem is to find $x = (x_1, x_2, ..., x_n)$ so as to minimize (or maximize) a nonlinear objective function subject to linear or nonlinear constraints:

$$
\begin{array}{llll}
\text{Minimize:} & z = f(x) & x = [x_1\, x_2\, ...\, x_n]^T & \\
\text{Subject to:} & h_i(x) = b_i & i = 1, 2, ..., m & (3.1) \\
 & G_j(x) \leq c_j & j = 1, 2, ..., r &
\end{array}
$$

x is an $(n \times 1)$ vector of decisions and the value $z = f(x)$ corresponds to the objective function, while $\{x |\ h_i(x) = b_i,\ G_j(x) \leq c_j\}$ defines the set of constraints. An optimum x^* is a feasible solution such that $f(x) \geq f(x^*)$ for any feasible x.

Nonlinear programming (NLP) problems are intrinsically more difficult to solve than LP and QP problems. Because of the possibility of multiple feasible regions and multiple locally optimal points within such regions, there is no known way to determine with certainty that the problem is infeasible, the objective unbounded, or that an optimal solution is the "global optimum" across all feasible regions.

3.3. Stochastic Programming

An extension of linear and mixed integer programming, called stochastic programming, is an attractive option for planning because it allows the decision maker to explicitly analyze uncertainties and control risks. The underlying idea is to simultaneously consider multiple scenarios of an uncertain future, each with an associated probability of occurrence. The model simultaneously determines an optimal contingency plan for each scenario and an optimal here-and-now plan that optimally hedges against these contingency plans. Optimization entails maximization or minimization of expected net profits or expected cost, where “expected” refers to multiplying net profits or costs associated with each scenario by their probability of occurrence.

Stochastic or probabilistic programming deals with situations where some or all of the parameters of the optimization problem are described by stochastic or random variables rather than by deterministic quantities. The resources of random variables can be several, depending on the nature and the type of the problem. For instance, in the design of concrete structures, the strength of concrete is a random variable since the compressive strength of concrete varies considerably from sample to sample. In the design of mechanical systems, the actual dimension of any machined part is a random variable since the dimension may lie anywhere within a specified and permissible tolerance band. Similarly, in the design of aircraft and rockets the actual loads acting on the vehicle depend on the atmospheric conditions prevailing at the time of the flight, which can not be predicted precisely in advance. Hence, the loads are to be treated as random variables in the design of such flight vehicles (Birge and Louveaux, 1997).

Depending on the nature of the equations involved, in terms of random variables in the problem, a stochastic optimization problem is called a stochastic linear, geometric, or nonlinear programming problem. The main idea used in stochastic programming is to convert the stochastic problem into an equivalent deterministic problem. The resulting deterministic problem is then solved by using known and familiar techniques such as linear, geometric, dynamic, and nonlinear programming.

Normally all decision processes involve uncertain information, particularly when future events are considered. Some known engineering examples are optimal control, real time optimization, process scheduling, production and capacity planning applications. Due to the inherently uncertain nature of wastewater networks, high economic incentives due to limitations in freshwater resources, and the environmental impact of industrial wastewater, the focus will be on designing flexible wastewater networks. Realistic water reuse and regeneration-reuse networks should be capable of accommodating perturbations in operating conditions as well as environmental regulations. Wastewater minimization applications can be developed with nonlinear programming models, which include parameter uncertainties characterized by probability distribution functions. Taking into consideration the uncertainty of key parameters, i.e. flow rates and concentrations, in application problems eliminate the possibility of unfeasible or non-applicable decisions.

A stochastic programming model brings into clearer focus the need to identify and incorporate contingency options for different types of scenario. In other words, the process of constructing a stochastic programming model encourages qualitative thinking about how to deal with unfavourable and favourable situations before they occur. An important strength of stochastic programming is that it allows explicit constraints to be imposed on the certain quantities such as limiting contaminant concentrations.

Stochastic programming is simply another name for the study of optimal decision making under uncertainty. This term emphasizes a link to mathematical programming and algorithmic optimization procedures. The applications in stochastic programming occur in a variety of areas of modelling uncertainty.

3.3.1. Decisions and Stages

Stochastic nonlinear programs are nonlinear programs in which some problem data may be considered uncertain. *Recourse programs* are those programs in which some decisions or recourse actions can be taken after uncertainty is disclosed. To be more precise, data uncertainty means that some of the problem data can be represented as random variables. An accurate probabilistic description of the random variables is assumed available, in the form of the probability distributions, densities or, more generally, probability measures (Brige and Louveaux, 1997).

Uncertainty is represented in terms of random experiments with outcomes denoted by ω. The set of all outcomes is represented by Ω. In studying wastewater minimization problems in refineries, for instance, the outcomes range from management and planning decisions to environmental concerns and economic priorities, while the random variables of interest may be the water demands or quality of crude feedstock. The relevant set of outcomes is clearly problem-dependent. Also, it is usually not very important to be able to define those outcomes accurately because the focus is mainly on their impact on some (random) variables. The particular values the various random variables will take are only known after the random experiment, i.e., the vector $\xi = \xi(\omega)$ is only known after the experiment.

The set of decisions is then divided into two groups:

i) A number of decisions have to be taken before the experiment. All these decisions are called *first-stage decisions*.

ii) A number of decisions can be taken after the experiment. These are called *second-stage decisions*.

First-stage decisions are represented by the vector x, while second-stage decisions are represented by the vector y or $y(\omega)$ or even $y(\omega, x)$ if one wishes to stress that second-stage decisions differ as functions of the outcome of the random experiment and of the first-stage decision. The sequence of events and decisions is thus summarized as $x \rightarrow \xi(\omega) \rightarrow y(\omega, x)$. Observe here that the definitions of first and second stages are only related to before and after the random experiment and may in fact contain sequences of decisions and events. In the wastewater minimization problem presented in the current study, the first stage corresponds to the total demand of freshwater during the whole time horizon. Second-stage decisions consist of volumes of wastewater reused or regenerated-reused for each of the assumed scenarios.

3.3.2. Two-Stage Program with Fixed Recourse

The stochastic approach presented in this section is normally used for the linear programming problem. This approach will be modified and used for the nonlinear programming model resulting from the wastewater minimization problem.

The two-stage stochastic linear program with fixed recourse is also known as *scenario analysis*. It is the problem of finding:

$$
\begin{aligned}
\min z = c^T x + E_\xi & \left[\min q(\omega)^T y(\omega)\right] \\
& s.t.\ Ax = b, \\
& T(\omega)x + Wy(\omega) = h(\omega), \\
& x \geq 0 \ and \ y(\omega) \geq 0
\end{aligned}
\tag{3.2}
$$

c = Objective function(over all cost)
^{T} = time horizon(summer/winter)
x = first stage variable(resuse flow)
E = mathematical expression
ξ = random variable(different temp 32,37,42)
Q / q = second stage value function
ω = random event(probability of occurrence different temp)
y = secondstage variable(fresh water flow/ regen flow)

As discussed above, a distinction is made between the first stage and the second stage. The first-stage decisions (like modifying the plant for reuse) are represented by the $(n_1 \times 1)$ vector x. Corresponding to x are the first-stage vectors (reuse) and matrices, c, b, and A, of sizes $(n_1 \times 1)$, $(m_1 \times 1)$, and $(m_1 \times n_1)$, respectively.

In the second stage, a number of random events(temperature changes) $\omega \in \Omega$ may realize. For a given realization *ω(probability of occurrence)*, the second-stage problem data $q(\omega)$, $h(\omega)$ and $T(\omega)$ become known, where $q(\omega)$ is $(n_2 \times 1)$, $h(\omega)$ is $(m_2 \times 1)$, and $T(\omega)$ is $(m_2 \times n_2)$.

Each component of q, T, and h is thus a possible random variable. Let $T_{i\cdot}(\omega)$ be the i^{th} row of $T(\omega)$. Piecing together the stochastic components of the second-stage data, we obtain a vector $\xi^T(\omega) = [q(\omega)^T, h(\omega)^T, T_{i\cdot}(\omega), \ldots, T_{m2\cdot}(\omega)]$, with potentially up to $N = n_2 + m_2 + (m_1 \times n_1)$ components. When the random event ω is realized, the second-stage problem data q, h, and T, become known. Then, the second-stage decision $y(\omega)$ or $y(\omega, x)$ must be taken.

The objective function of (3.2) contains a deterministic term $c^T x$ (solution of the deterministic model) and the expectation of the second-stage objective $q(\omega)^T y(\omega)$ (impact due to second stage variable) taken over all realizations of the random event ω. This second-stage term is the more difficult one because, for each ω (temperature), the value y(ω)(out come of the second stage event) is the solution of a linear program. To stress this fact, one sometimes uses the notion of a deterministic equivalent program. For a given realization ω, let

$$Q(x,\xi(\omega)) = \min_y \left\{ q(\omega)^T y \mid Wy = h(\omega) - T(\omega)x, y \geq 0 \right\} \tag{3.3}$$

be the second-stage value function. Then, define the expected second-stage value function

$$Q(x) = E_{\xi}Q(x, \xi(\omega)) \tag{3.4}$$

and the deterministic equivalent program (DEP)

$$\begin{aligned} \min z &= c^T x + Q(x) \\ s.t.\ Ax &= b, \\ x &\geq 0 \end{aligned} \tag{3.5}$$

This representation of a stochastic program clearly illustrates that the major difference from a deterministic formulation is in the second-stage value function. Many variable (vectors) like impurities concentration ,capacity utilization , pressure , cost of individual components are used .

3.4. Optimization Software

Commercial packages for optimizing nonlinear and mixed integer programming problems have been available for decades. The first LP packages appeared during the late 1950s and the first MIP packages appeared during the early 1970s (Shapiro, 2001). Since then, their capabilities have evolved with advances in information technology. Optimization of LP, MIP and NLP models on today's PCs is significantly faster, measured in millions of instructions per second (MIPS), than it was on mainframes of 10 years ago, which cost several thousand times more in constant dollars. At the time, the scope of optimization packages has expanded greatly to include algebraic languages for model generation and routines for managing data and implementing user interfaces. The growing interest in optimization of complex and large-scale planning problems is due in no small part to these incredible substantial technological advances.

Optimizers are packages containing numerical algorithms that analyze a given matrix representation of a non linear or mixed integer programming model to produce an optimal, or near optimal solution. An optimizer is called as a subroutine in an optimization modelling system. On the other hand, an *algebraic modelling language development kit* has three components:

a. an algebraic modelling language interpreter,

b. an optimizer, and

c. database drivers.

The algebraic modelling language permits the user to specify the mathematical form of an optimization model using an algebraic syntax similar to what he or she would use when writing out a model statement by hand. To test the consistency of the model statement, the user also specifies a data set describing a model instance. The system reads the model statement and the data set and attempts to interpret it as a well-defined non linear or mixed integer programming model. If the interpretation is successful, it attempts to populate the matrix it has created with the given data. If the data set is consistent both internally and with the algebraic modelling specification, the interpreter creates a matrix representation of the model. The user must then check this matrix to ensure that it is a valid representation of the optimization problem to be analyzed.

3.4.1. NLP Packages and Solvers

Almost all NLP packages employ systems with higher level user interfaces, such as spreadsheets and algebraic modelling systems. All such systems have at their core, adaptations of one or more "stand-alone" optimization packages. By stand-alone we mean software designed specifically to accept the specifications of a nonlinear program, attempt to solve it, and return the results of that attempt to the user or to an invoking application. The NLP capabilities and characteristics of those higher level systems therefore naturally derive from those of their incorporated optimizers.

Most existing NLP optimizers are FORTRAN-based. Most are capable of operation as true stand-alone systems or as subsystems that are embedded in larger systems and solve problems generated by, or posed through, those systems. All NLP optimizers require that the user supply the following:

- A specification of the NLP problem to be solved – at a minimum, the number of functions, the number of variables, which function is the optimization objective, bounds on the functions and variables, and initial values of some or all variables. The system may supply default initial values, but specifying them is recommended.

• One or more subprograms that supply to the optimizer, on demand, the values of the functions for a specified set of variable values. Some systems also allow the user the option of supplying derivative values.

3.4.1.1. Stand-Alone Packages

a) GRG-Based Optimizers

The optimizers used in solving the deterministic models in Chapter 5 are CONOPT and MINOS. Both optimizers are called from General Algebraic Modelling System (GAMS). Below is a brief description of three famous and widely used NLP optimizers. GAMS will be introduced in more detail further in this chapter.

GRG2. This code is presently the most widely used for the generalized reduced gradient method. In addition to its use as a stand-alone system, it is the optimizer employed by the "Solver" optimization options within the spreadsheet programs Microsoft Excel, Novell's Quattro Pro, Lotus 1-2-3, and the GINO interactive solver.

CONOPT. This is another widely used implementation of the GRG algorithm. It is designed to solve large, sparse problems. CONOPT is available as a stand-alone system or callable subsystem. It is one of the optimizers callable by the GAMS system.

MINOS. This system employs a modified augmented Lagrangian algorithm (Edgar et al., 2001). MINOS uses sparse matrix representation throughout and is capable of solving nonlinear problems exceeding 1000 variables and rows. MINOS is the default optimizer option under GAMS system for both linear and nonlinear problems.

b) Mathematical Software Libraries

Many of the major callable libraries of mathematical software include at least one general NLP component (i.e. capable of solving problems with nonlinear constraints). IMSL provides individual callable routines for most variations of linear and nonlinear constraints and objectives. Another software library is the NAG FORTRAN Library which is also available as a toolbox of MATLAB.

3.4.1.2. Spreadsheet Optimizers

In the 1980s, a major move away from FORTRAN and C optimization began as optimizers were interfaced to spreadsheet systems for desktop computers (Edgar et al., 2001). The spreadsheet has become, de facto, the universal user interface for entering and manipulating numeric data.

The *Excel Solver* is embedded in Excel and supplied by Frontline, a third party company which provides also an extended (professional) version of the solver. Beginning with version 3.0 in 1991, Excel incorporated an NLP solver and later version 4.0 included an LP solver and mixed-integer programming (MIP) capability for both linear and nonlinear problems. The user specifies a set of cell addresses to be independently adjusted (the decision variables), a set of formula cells whose values are to be constrained (the constraints), and a formula cell designated as the optimization objective. The solver uses the spreadsheet interpreter to evaluate the constraint and objective functions, and approximate derivatives, using finite differences. The NLP solution engine for the Excel solver is GRG2.

3.4.1.3. Algebraic Modelling Systems

An algebraic modelling system normally accepts the specification of a model in text as a system of algebraic equations. The system parses the equations and generates a representation of the expressions that can be numerically evaluated by its interpreter. In addition, some analysis is done to determine the structure of the model and to generate expressions for evaluating the Jacobian matrix. The processed model is then available for presentation to an equation solver or optimizer.

Since NLP optimization problems are difficult to solve, a number of universities and research institutions are engaged in optimization research and its applications. These include Carnegie Mellon, Imperial College, Princeton and Purdue Universities. Optimization software and tools that are widely accepted by the optimization community and proved effective in solving process engineering optimization problems are:

i) AMPL: Bell Labs (http://www.bell-labs.com/)

ii) CPLEX: ILOG Consulting Group (http://www.ilog.fr/corporate/support/)

iii) GAMS: GAMS Inc., Washington D.C., US (http://www.gams.com)

iv) LINDO: LINDO systems Inc. (http://www.lindo.com)

v) MathPro 2000: (http://sundown-vmp.com/mathpro)

vi) OSL: IBM Business Consulting (http://www.ibm.com/services/buscon/)

vii) XPRESS-MP: Dash Association, Ltd., England (http://www.dash.co.uk)

viii) PIMS: Aspen Tech. (http://www.aspentec.com)

The optimization software used to solve the wastewater optimization models developed in the current study is GAMS. The main features and capabilities of GAMS are highlighted below.

3.5. GAMS Optimization Software

GAMS (the acronym stands for General Algebraic Modelling System) is an optimization software that can be utilized to construct and solve large and complex mathematical programming models. The user's guide of GAMS summarizes the main features of GAMS as (Brooke et al., 1998):

a) Providing a high-level language for the compact representation of large and complex models.

b) Allowing changes to be made in model specifications simply and safely.

c) Allowing unambiguous statements of algebraic relationships.

d) Permitting model descriptions that are independent of solution algorithms.

GAMS has incorporated ideas drawn from relational database theory and mathematical programming and has attempted to merge these ideas to suit the needs of strategic modellers. Relational database theory provides a structured framework for developing general data organization and transformation capabilities. Mathematical programming provides a way of describing a problem and a variety of methods for solving it. GAMS has been selected as the main optimization solver for the current work due to a number of attractive features, which are summarized in the following paragraphs.

i) A number of algorithmic methods are readily available and can be applied without changing the user's model representation. Implementation of alternative methods is quite easy and may be achieved by just specifying the solver name, without changes in existing model representation. A number of solvers for handling linear, nonlinear, mixed integer, and mixed integer nonlinear problems (listed below) are available and licensed by GAMS Inc.

ii) The optimization problem is expressible independently of the data it uses. This separation of logic and data allows a problem to be increased in size without causing an increase in the complexity of the representation.

iii) The use of the relational data model requires that the allocation of computer resources be automated. This means that large and complex models can be constructed without the user having to worry about details such as array sizes and scratch storage.

iv) The GAMS model representation is in a form that can be easily read and interpreted by people. This means that the GAMS program itself is the documentation of the model. A GAMS model representation is concise, and makes full use of the elegance of the mathematical representation.

v) All data transformations are specified concisely and algebraically. This means that all data can be entered in their most elemental form and that all transformations made in constructing the model and in reporting are available for inspection.

vi) Explanatory text can be made part of the definition of all symbols and is reproduced whenever associated values are displayed. All information needed to understand the model is in one document.

vii) The basic GAMS system is file-oriented and no special editor or graphical input and output routines exist. Rather than burden the user with having to learn yet another set of editing commands, GAMS offers an open architecture in which a word processor or any ASCII file editor can be used.

viii) Optimization results can be displayed at different levels of details. The user may select to list extensive report giving the values of all variables, or displaying just selected values. At problem formulation stage, it may be useful to list the solver-specific parameters and detailed results for every iteration.

ix) In its recent implementation, GAMS (V. 20.5 130) is licensed with GAMS IDE, which is a general text editor with the ability to launch and monitor the compilation and execution of GAMS models. Progress of compilation and execution can be monitored in the process window. The process window is also used as a navigation tool to locate syntax errors in the source code and to find various anchor points in the listing file. The IDE also facilitates the selection of default solvers and manages GAMS parameters on a file by file basis

Besides the advantages listed above, and the solving power of GAMS, perhaps the main limitation faced was the difficulty in representing the output results as plots or graphs. For instance, transferring the output results to Microsoft Excel is a time consuming exercise, especially for large-scale problems and when running a large number of case studies. Spreadsheet based optimization packages, such as PIMS, may be used in order to overcome this limitation. But such packages might provide limited solver capabilities and less optimization methods.

Various types of problems can be solved with GAMS. The type of model must be known before it is solved. GAMS checks the model type and issues explanatory error messages in case of mismatch. The problem types which are realized by GAMS are:

1. ***LP***: Linear programming. There are no nonlinear terms or discrete (binary or integer) variables in the model.

2. ***NLP***: Nonlinear programming. There are general nonlinear terms involving only "smooth" functions in the model, but no discrete variables.

3. ***DNLP***: Nonlinear programming with discontinuous derivatives. This is the same as NLP, except that 'non-smooth' functions can appear as well. These are more difficult to solve than normal NLP problems.

4. ***RMIP***: Relaxed mixed integer programming. The model can contain discrete variables but the discrete requirements are relaxed, meaning that the integer and binary variables can assume any values between their bounds.

5. ***MIP***: Mixed integer programming. Like RMIP but the discrete requirements are enforced: the discrete variables must assume integer values between their bounds.

6. ***RMINLP***: Relaxed mixed integer nonlinear programming. The model can contain both discrete variables and general nonlinear terms. The discrete requirements are relaxed. This class of problem is the same as NLP in terms of difficulty of solution.
7. ***MINLP***: Mixed integer nonlinear programming. Characteristics are the same as for RMINLP, but the discrete requirements are enforced.
8. ***MPEC***: Mathematical programs with equilibrium constraints.
9. ***MCP***: Mixed Complementarily Problem.
10. ***CNS***: Constrained Nonlinear System.

For each of the problem types outlined above, GAMS provides a number of solvers that are capable of handling the problem. The user is given the option of using the default solver or selecting a specific solver.

3.6. Conclusion

Two types of mathematical models, namely, a ***deterministic model*** and a ***stochastic model*** are required to be developed for the current work. Mathematical deterministic models are used for problems in which the variables are known and specified. Alternatively, stochastic model are used for decision making under uncertainty. Generally, the model for optimizing wastewater networks is nonlinear in nature and the nonlinearity mainly arises from multiplying the water flow rate with the concentration of the contaminants.

GAMS (General Algebraic Modelling System) is the optimization solver chosen for solving the proposed optimization models. This software has the flexibility to construct and solve large and complex mathematical programming models easily. Further, various types of problems can be solved with GAMS and for each of the problem types, GAMS provides a number of solvers that are capable of handling the problem. The user has the option of using the default solver or selecting a specific solver. GAMS checks the model type and issues explanatory error messages in case of mismatch.

Based on the above and the number of attractive features as listed in section 3.5 of this chapter, GAMS has been selected as the main optimization solver for the current work.

Chapter Four

4. OPTIMIZATION MODELS

4.1. Introduction

The main objective of this chapter is to develop a mathematical model to optimize water-using networks for industrial water reuse and wastewater minimization. The proposed model will be considered as a deterministic model, which will be modified later to introduce uncertainties in key parameters. This will result in a stochastic optimization model capable of analyzing, synthesizing and retrofitting industrial wastewater networks subjected to uncertainties in operational, economical and environmental parameters.

The deterministic model derived in this chapter is based on the superstructure model proposed by a number of researchers and presented by Mann and Liu (1999).

4.2. Mathematical Model

An industrial water-using unit is shown schematically in Figure 4.1. A water-using unit receives freshwater in addition to recycled water streams from other units and regenerators. Furthermore, certain units utilize steam as a direct contact with the hydrocarbons (crude) for stripping and heating purposes. Condensed steam is considered as a wastewater source (sour water) because it contains contaminants transferred from the feedstock of the processing unit. Effluents from the water-using unit may be directed to three possible destinations: to other units as direct reuse, to the regeneration units for partial removal of selected contaminants, or to wastewater treatment for disposal. Other nodes of the wastewater network correspond to the regeneration operations. A regeneration unit is shown in Figure 4.2. This unit receives wastewater streams from the water-using units as well as from other regeneration units for further removal of contaminants. Effluents from the regeneration units are recycled back to the water-using units, sent to other regeneration operations, or to the wastewater treatment and disposal plant.

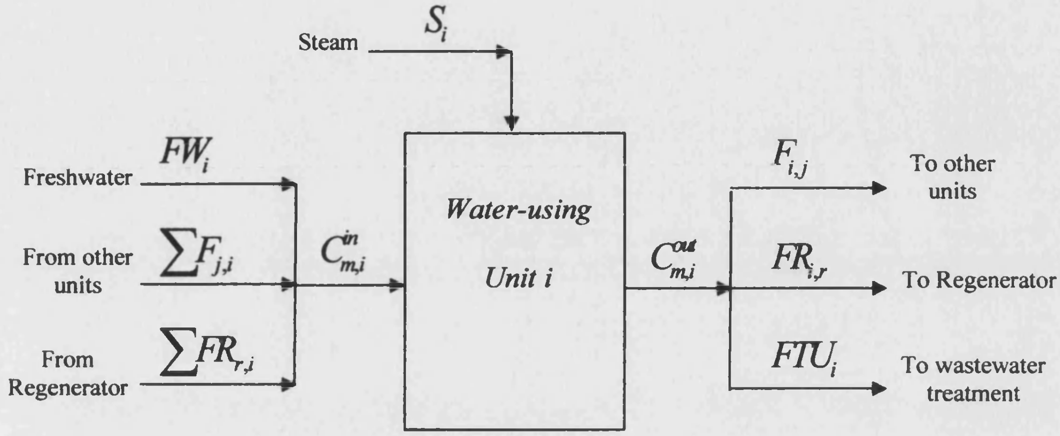


Figure 4.1: Input/output structure of a general water-using unit applicable to a refinery.

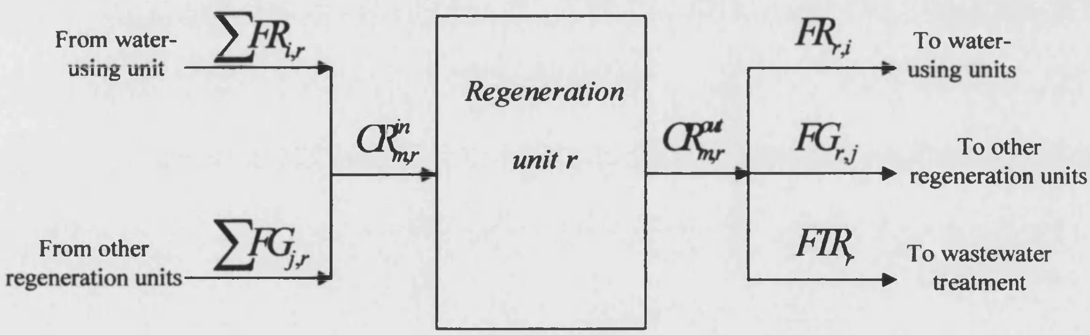


Figure 4.2: Input/output structure of a general regeneration unit

Consider a set of N water-using units and R regeneration units. An overall material balance for a water-using unit, i, can be expressed as:

$$FW_i + S_i + \sum_{\substack{j=1\\ j\neq i}}^{N} F_{j,i} + \sum_{r=1}^{R} FR_{r,i} = \sum_{\substack{j=1\\ j\neq i}}^{N} F_{i,j} + \sum_{r=1}^{R} FR_{i,r} + FTU_i \qquad \forall i \in N \tag{4.1}$$

Where FWi and Si are freshwater and steam flow rates to unit i, respectively. Fi,j is water reuse from unit i to unit j, FRr,i is the flow rate of regenerated water from regenerator r to unit i, FRi,r is the wastewater flow rate from unit i to regenerator r, whilst FTUi is the wastewater flow rate from unit i to the wastewater treatment and disposal unit.

Similarly, an overall material balance for a regeneration unit, r, can be expressed as:

$$\sum_{i=1}^{N} FR_{i,r} + \sum_{\substack{j=1\\ j\neq r}}^{R} FG_{j,r} = \sum_{i=1}^{N} FR_{r,i} + \sum_{\substack{j=1\\ j\neq r}}^{R} FG_{r,j} + FTR_r \qquad \forall r \in R \tag{4.2}$$

Where $FG_{j,r}$ is the flow rate of water from regenerator j to another regenerator r for further regeneration and treatment, and FTR_r is the wastewater flow rate from regenerator r to the wastewater treatment and disposal unit.

The difference between the input and output concentrations of the contaminats, entering and leaving a water-using unit, is proportional to the mass load of contaminant that is transferred from the waste stream to the water stream. Hence, for a set of M contaminants, a component balance for contaminant, m, for the water-using unit, i, can be expressed as:

$$C_{m,i}^{out} = C_{m,i}^{in} + \frac{\Delta w_{m,i} \times 10^3}{FW_i + S_i + \sum_{\substack{j=1\\ j\neq i}}^{N} F_{j,i} + \sum_{r=1}^{R} FR_{r,i}} \qquad \forall i \in N, \forall m \in M \tag{4.3}$$

Here, $C_{m,i}^{in}$ and $C_{m,i}^{out}$ are the input and output concentrations of contaminant m of water-using unit, i. $\Delta w_{m,j}$ is the mass load of contaminant m removed from unit i. Concentrations are expressed in ppm, mass loads in kg/hr, and flow rates in tonnes/hr.

Concentration relationships can be calculated based on fixed pickup model as indicated above (fixed amount of impurities will be transferred to water irrespective of inlet concentration and the process parameters) or the fixed bulk concentration model (the outlet concentration of water is fixed based on thermodynamic equilibrium). Therefore either outlet concentration is assumed and mass pick up is calculated or mass pick up is assumed and outlet concentration is calculated.

The average inlet concentration of contaminant *m* can be expressed as:

$$C_{m,i}^{in} = \frac{\sum_{\substack{j=1 \\ j \neq i}}^{N} F_{j,i} C_{m,j}^{out} + \sum_{r=1}^{R} FR_{r,i} C_{m,r}^{out}}{FW_i + \sum_{\substack{j=1 \\ j \neq i}}^{N} F_{j,i} + \sum_{r=1}^{R} FR_{r,i}} \qquad \forall i \in N, \forall m \in M \qquad (4.4)$$

For a regeneration unit *r*, the outlet concentration of contaminant *m* is equal to the inlet concentration less the amount removed.

$$CR_{m,r}^{out} = CR_{m,r}^{in} - \frac{\Delta w_{m,r} \times 10^3}{\sum_{i=1}^{N} FR_{i,r} + \sum_{\substack{j=1 \\ j \neq r}}^{R} FG_{j,r}} \qquad \forall r \in R, \forall m \in M \qquad (4.5)$$

$\Delta w_{m,r}$ represents the mass load of contaminant *m* removed from the wastewater stream. Moreover, the inlet concentration of contaminants can be expressed as:

$$CR_{m,r}^{in} = \frac{\sum_{i=1}^{N} FR_{i,r} C_{m,i}^{out} + \sum_{\substack{j=1 \\ j \neq r}}^{R} FG_{j,r} C_{m,r}^{out}}{\sum_{i=1}^{N} FR_{i,r} + \sum_{\substack{j=1 \\ j \neq r}}^{R} FG_{j,r}} \qquad \forall r \in R, \forall m \in M \qquad (4.6)$$

4.3. Deterministic Optimization Model

The optimization model is based on minimizing the total cost of the wastewater network. The cost items include: freshwater cost, water recycle/reuse cost, partial wastewater regeneration cost, and wastewater treatment and disposal cost. For a set of N water-using units and R regeneration units, the objective function may be defined as:

$$Min\left\{C_{FW}\sum_{i=1}^{N}FW_i+C_{RU}\sum_{i=1}^{N}\sum_{\substack{j=1\\j\neq i}}^{N}F_{i,j}+C_{RW}\sum_{r=1}^{R}\sum_{i=1}^{N}FR_{r,i}+C_{WT}\left(\sum_{i=1}^{N}FTU_i+\sum_{r=1}^{R}FTR_r\right)\right\} \tag{4.7}$$

where CFW, CRU, CRW, and CWT are unit costs (KD/tonne) of freshwater, wastewater reuse, regeneration-reuse, and wastewater treatment and disposal, respectively. At current exchange rates, one KD (Kuwaiti Dinar) is equivalent to US$ 3.3. FWi is freshwater demanded by unit i, Fi,j is flow rate of direct water reuse from unit i to unit j, and FRr,i is flow rate of regenerated water by regenerator r to unit i. FTUi and FTRr are flow rates of wastewater streams from unit i and regeneration unit r, respectively to wastewater treatment and disposal plants.

The objective function expressed by Equation 4.7 is subject to the following constraints:

a) Inlet Concentrations

Inlet concentrations of contaminants should not exceed the maximum allowable concentration, $C_{m,i}^{in,\max}$, at the inlet of a water-using unit, i:

$$C_{m,i}^{in}\leq C_{m,i}^{in,\max} \tag{4.8}$$

Substituting the value of $C_{m,j}^{in}$, which is expressed by Equation 4.4 above:

$$C_{m,i}^{in}=\frac{\sum\limits_{\substack{j=1\\j\neq i}}^{N}F_{j,i}C_{m,j}^{out}+\sum\limits_{r=1}^{R}FR_{r,i}C_{m,r}^{out}}{FW_i+\sum\limits_{\substack{j=1\\j\neq i}}^{N}F_{j,i}+\sum\limits_{r=1}^{R}FR_{r,i}}\leq C_{m,i}^{in,\max}\qquad \forall i\in N,\forall m\in M \tag{4.9}$$

Rearranging Equation (4.9), this constraint becomes:

$$FW_i C_{m,i}^{in,\max} + \sum_{\substack{j=1 \\ j\neq i}}^{N} F_{j,i}\left[C_{m,i}^{in,\max} - C_{m,j}^{out}\right] + \sum_{r=1}^{R} FR_{r,i}\left[C_{m,i}^{in,\max} - C_{m,r}^{out}\right] \geq 0 \qquad \forall i \in N, \forall m \in M \tag{4.10}$$

b) Outlet Concentrations

To maximize water reuse, the outlet concentration of contaminants from a water-using unit is forced to be equal to a limiting outlet concentration. This limiting outlet concentration may be specified based on a number of considerations, such as solubility limits, operating conditions, in addition to regeneration and process design limits. Hence, the maximum outlet concentration of contaminants will be forced to be equal to a pre-specified limit, $C_{m,i}^{out,\max}$.

$$C_{m,i}^{out} = C_{m,i}^{out,\max} \tag{4.11}$$

Substituting the value of $C_{m,j}^{out}$, which is expressed by Equation 4.3 above:

$$C_{m,i}^{out} = C_{m,i}^{in} + \frac{\Delta w_{m,i} \times 10^3}{FW_i + S_i + \sum_{\substack{j=1 \\ j\neq i}}^{N} F_{j,i} + \sum_{r=1}^{R} FR_{r,i}} = C_{m,i}^{out,\max} \qquad \forall i \in N, \forall m \in M \tag{4.12}$$

Substituting $C_{m,i}^{in}$ from Equation 4.4 and rearranging, the outlet concentration constraint becomes:

$$\left(FW_i + S_i + \sum_{\substack{j=1 \\ j\neq i}}^{N} F_{j,i} + \sum_{r=1}^{R} FR_{r,i}\right)\left(C_{m,i}^{in} - C_{m,i}^{out,\max}\right) = \Delta w_{m,i} \times 10^3 \qquad \forall i \in N, \forall m \in M \tag{4.13}$$

c) Concentration Limits of Regenerated Water

A regeneration unit is required to reduce the concentration of specific contaminant(s) to a pre-specified minimum limit, $CR_{m,r}^{out,\min}$:

$$CR_{m,r}^{out} = C_{m,r}^{out,\min} \tag{4.14}$$

$CR_{m,r}^{out}$ is expressed by Equation 4.5, hence, Equation 4.14 becomes:

$$CR_{m,r}^{out} = CR_{m,r}^{in} - \frac{\Delta w_{m,r} \times 10^3}{\sum_{i=1}^{N} FR_{i,r} + \sum_{\substack{j=1 \\ j \neq r}}^{R} FG_{j,r}} = CR_{m,r}^{out,\min} \quad \forall r \in R, \forall m \in M \tag{4.15}$$

Substituting $CR_{m,r}^{in}$ from Equation 4.6 into Equation 4.15 and rearranging, this constraint becomes:

$$\sum_{i=1}^{N} FR_{i,r} \left(C_{m,r}^{out,\min} - C_{m,i}^{out} \right) + \sum_{\substack{j=1 \\ j \neq r}}^{R} FG_{j,r} \left(C_{m,r}^{out,\min} - C_{m,j}^{out} \right) = -\Delta w_{m,r} \times 10^3 \quad \forall r \in R, \forall m \in M \tag{4.16}$$

$FG_{j,r}$ is the wastewater flow rate from regenerator j to another regenerator r.

d) Material Balance for Water Using Units

The material balance for the water-using unit (Equation 4.1) can be rearranged and expressed as:

$$FW_i + S_i + \sum_{\substack{j=1 \\ j \neq i}}^{N} \left(F_{j,i} - F_{i,j} \right) + \sum_{r=1}^{R} \left(FR_{r,i} - FR_{i,r} \right) - FTU_i = 0 \quad \forall i \in N \tag{4.17}$$

e) Material Balance for Regeneration Units

The material balance for the regeneration unit (Equation 4.2) can be rearranged and expressed as::

$$\sum_{i=1}^{N}\left(FR_{i,r}-FR_{r,i}\right)+\sum_{\substack{j=1\\j\neq r}}^{R}\left(FG_{j,r}-FG_{r,j}\right)-FTR_{r}=0 \qquad \forall r\in R \tag{4.18}$$

f) Positive Variables

All concentrations and flow rates should be positive:

$$\begin{array}{lll} FW_i & \geq 0 & \forall i\in N \\ S_i & \geq 0 & \forall i\in N \\ F_{i,j} & \geq 0 & \forall i,j\in N \\ FR_{r,j} & \geq 0 & \forall i\in N,\forall r\in R \\ FG_{r,j} & \geq 0 & \forall r,j\in R \\ FTU_i & \geq 0 & \forall i\in N \\ FTR_r & \geq 0 & \forall r\in R \\ C_{m,j}^{in} & \geq 0 & \forall m\in M,\forall i\in N \\ C_{m,j}^{out} & \geq 0 & \forall m\in M,\forall i\in N \\ C_{m,r}^{out} & \geq 0 & \forall m\in M,\forall r\in R \end{array} \tag{4.19}$$

4.4. Stochastic Optimization Model

For the wastewater minimization problem considered in this study, two types of problems may be identified. The first one involves designing the network, while the second problem involves decisions on the inventories (flow rates) for fixed freshwater resources. These problems will be termed as "Stochastic Design" and "Stochastic Operational" problems. For the former, direct wastewater reuse may be considered as the first-stage decision variable, whilst freshwater demands and regeneration-reuse amounts are the second-stage variables. Stochastic operational solutions are needed for cases when resources are limited, as well as for planning purposes. For these instances, it would be useful to determine the optimal freshwater demands that will minimize the cost of the wastewater network in the presence of uncertainties. In this case, freshwater demands will be considered as the first-stage decision variables, whilst reuse and regeneration-reuse amounts are the second-stage decision variables.

Stochastic design problems are more effective in developing resilient wastewater networks, and at the same time applicable for both grassroots' design and retrofit problems. Nonetheless, operational stochastic problems may be applied on existing wastewater networks to study variations in freshwater demands and capacities of regeneration and treatment plants.

For the wastewater minimization problem presented in the current study, the stochastic optimization model will be derived for the stochastic design problem. In this model, uncertainty is introduced through the assumption that the random variables emerge from three scenarios, namely, "low", "normal", or "high". The "low" and "high" scenarios, for instance, may be assumed to be a 5% decrease or increase in the nominal (design level) load of contaminants, respectively. It is useful here to index these decisions by a scenario index s = 1, 2, 3 corresponding to "low", "normal", or "high" conditions, respectively.

First-stage decisions are considered to be the amounts of wastewater reuse, Fi,j, whilst freshwater demand, FWi, regeneration-reuse, FRr,i, and the amounts sent to the wastewater treatment and disposal plant, FTUi and FTRr, are considered as second-stage decisions. This creates a new set of variables of the form FW_i^s, FTU_i^s and FTR_r^s. For example, FW_4^3 represents the volume of freshwater demanded by unit '4', when the level of contaminants, for instance, is higher than the normal level.

The probability of occurrence is defined for each scenario by the set Eω = {ω1, ω2, ω3}, where ω1+ω2+ω3= 1. Consequently, the objective function of the stochastic model may be derived from the deterministic objective function (Equation 4.7) and represented as follows:

$$Min\left\{\begin{array}{l} C_{FW}\sum_{s=1}^{3}\sum_{i=1}^{N}\omega_s FW_i^s + C_{RU}\sum_{i=1}^{N}\sum_{\substack{j=1\\ j\neq i}}^{N}F_{i,j} + \\ C_{RW}\sum_{s=1}^{3}\sum_{r=1}^{R}\sum_{i=1}^{N}\omega_s FR_{r,i}^s + C_{WT}\sum_{s=1}^{3}\omega_s\left(\sum_{i=1}^{N}FTU_i^s + \sum_{r=1}^{R}FTR_r^s\right) \end{array}\right\} \tag{4.20}$$

This stochastic objective function minimizes the cost of the wastewater network while accounting for the possibility of occurrence of the s scenarios. However, it would result in only one decision concerning the direct reuse variable, Fi,j.

Similarly, the constraints should be modified and represented in terms of the first- and second-stage decision variables. The maximum allowable concentration constraints (Equations 4.10) may be defined for the three scenarios (s = 1, 2, 3) as:

$$\begin{aligned} & FW_i^s C_{m,i}^{in,\max} + \sum_{\substack{j=1 \\ j\neq i}}^{N} F_{j,i}\left[C_{m,i}^{in,\max} - C_{m,j}^{out,s}\right] + \\ & \sum_{r=1}^{R} FR_{r,i}^s \left[C_{m,i}^{in,\max} - C_{m,r}^{out,s}\right] \geq 0 \end{aligned} \qquad \begin{aligned} \forall i \in N, \forall m \in M \\ s = 1,2,3 \end{aligned} \qquad (4.21)$$

Operational uncertainties directly affect the mass load of contaminants, $\Delta w_{m,i}$, transferred from the units to the water streams. Hence, the stochastic model would result in different mass loads for different scenarios. Accordingly, $\Delta w_{m,i}^s$ is introduced and constraint (4.13) is expressed in terms of the three scenarios as:

$$\begin{aligned} & \left(FW_i^s + S_i + \sum_{\substack{j=1 \\ j\neq i}}^{N} F_{j,i} + \sum_{r=1}^{R} FR_{r,i}^s\right)\left(C_{m,i}^{in,s} - C_{m,i}^{out,\max}\right) \\ & = \Delta w_{m,i}^s \times 10^3 \end{aligned} \qquad \begin{aligned} \forall i \in N, \forall m \in M \\ s = 1,2,3 \end{aligned} \qquad (4.22)$$

Note that, in the current implementation, the steam amounts, Si, are assumed to be constant to satisfy the stripping requirements of the processes. The stochastic version of constraints 4.16 to 4.19 may be similarly represented as:

$$\begin{aligned} & \sum_{i=1}^{N} FR_{i,r}^s \left(C_{m,r}^{out,\min} - C_{m,i}^{out,s}\right) + \\ & \sum_{\substack{j=1 \\ j\neq r}}^{R} FG_{j,r}^s \left(C_{m,r}^{out,\min} - C_{m,j}^{out,s}\right) = -\Delta w_{m,r}^s \times 10^3 \end{aligned} \qquad \begin{aligned} \forall r \in R, \forall m \in M \\ s = 1,2,3 \end{aligned} \qquad (4.23)$$

$$FW_i^s + S_i + \sum_{\substack{j=1 \\ j\neq i}}^{N}\left(F_{j,i} - F_{i,j}\right) + \sum_{r=1}^{R}\left(FR_{r,i}^s - FR_{i,r}^s\right) - FTU_i^s = 0 \qquad \forall i \in N, s = 1,2,3 \qquad (4.24)$$

$$\sum_{i=1}^{N}\left(FR_{i,r}^{s}-FR_{r,i}^{s}\right)+\sum_{\substack{j=1\\j\neq r}}^{R}\left(FG_{j,r}^{s}-FG_{r,j}^{s}\right)-FTR_{r}^{s}=0 \quad \forall r\in R, s=1,2,3 \tag{4.25}$$

$$\begin{array}{lll}
FW_{i}^{s} & \geq 0 & \forall i\in N, s=1,2,3 \\
S_{i} & \geq 0 & \forall i\in N \\
F_{i,j}^{s} & \geq 0 & \forall i,j\in N, s=1,2,3 \\
FR_{r,j}^{s} & \geq 0 & \forall i\in N, \forall r\in R, s=1,2,3 \\
FG_{r,j}^{s} & \geq 0 & \forall r,j\in R, s=1,2,3 \\
FTU_{i}^{s} & \geq 0 & \forall i\in N, s=1,2,3 \\
FTR_{r}^{s} & \geq 0 & \forall r\in R, s=1,2,3 \\
C_{m,j}^{in,s} & \geq 0 & \forall m\in M, \forall i\in N, s=1,2,3 \\
C_{m,j}^{out,s} & \geq 0 & \forall m\in M, \forall i\in N, s=1,2,3 \\
C_{m,r}^{out,s} & \geq 0 & \forall m\in M, \forall r\in M, s=1,2,3
\end{array} \tag{4.26}$$

Both the deterministic and stochastic optimization models are NLP formulations which have been solved using the CONOPT2 solver within GAMS (Brooke et al., 1998).

4.5. Conclusion

Two types of mathematical models, a *deterministic model* and a *stochastic model* were developed for the current work. The variables / limits such as maximum allowable inlet concentration of contaminants in water using units, limiting outlet concentration of water using units and the concentration limits of contaminants from Regeneration unit etc were specified for the mathematical deterministic models. deterministic model incorporating various constraints is arrived with the objective function of minimizing cost.

Stochastic model is developed for decision making under uncertainty. Uncertainty will be introduced through the assumption that the random variables emerge from three scenarios namely, “low”, “normal” and “high”. Model will be validated using the actual data for the plant in the subsequent chapters.

Chapter Five

5. SOLUTION OF THE DETERMINISTIC OPTIMIZATION MODEL

5.1 Introduction

As discussed in Chapter 1, refineries are principal industrial water consumers and hence they generate large volumes of wastewater. Refinery facilities consist of sophisticated networks of process units, which are generally integrated depending on the units operated to meet the product slate and the final economic requirement. This Chapter considers wastewater minimization in oil refineries. A number of case studies will be presented to validate and demonstrate the capabilities of the deterministic mathematical model presented in Chapter 4. A case study representing a wastewater network in a typical refinery will be presented. This case study will be solved using the deterministic model. In the later Chapters, the same case study will be used for sensitivity analysis as well as for solving the stochastic optimization model.

5.2 Examples from Literature

It is vital to validate the proposed mathematical models before introducing uncertainties and solving the stochastic models. For this reason, a number of case studies have been collected from literature, solved and compared. The literature case studies include:

1. Example-1: Three operations, three contaminants.
2. Example-2: Four operations, three contaminants.
3. Example-3: Eight operations, four contaminants

5.2.1 Example One

This example considers a simplified data set from a petroleum refinery cited by a number of researchers including Wang and Smith (1994), Doyle and Smith (1997), Bagajewicz (2000) and Savelski and Bagajewicz (2003). In this example, three water using operations and three contaminants are considered. Limiting process data is given in Table 5.1. Mass loads were determined from the limiting freshwater flow rates and the concentration limits.

Table 5.1: Process limiting data for Example-1.

Operation	Contaminants	Limiting Freshwater (tonnes/hr)	C_{in}^{max} (ppm)	C_{out}^{max} (ppm)	Load (kg/hr)
1	Hydrocarbon	45	0	15	0.675
	H_2S		0	400	18.0
	Salt		0	35	1.575
2	Hydrocarbon	34	20	120	3.4
	H_2S		300	12,500	414.8
	Salt		45	180	4.59
3	Hydrocarbon	56	120	220	5.6
	H_2S		20	45	1.4
	Salt		200	9,500	520.8

The deterministic optimization model was utilized for solving Example-1. Regeneration-reuse is not allowed for this example. The model was solved for the reuse option only. Limiting freshwater flow rates were used as upper limits. Without applying any constraints, the model produced the optimum wastewater network shown in Figure 5.1. The resulting network is identical to the one reported in the literature (e.g. Doyle and Smith, 1997; Savelski and Bagajewicz, 2003). It can be seen that the connection from operation 3 to operation 2 is particularly small, showing a reuse of only 0.067 tonnes/hr, which would be uneconomic. Adding a constraint to forbid reuse from operation 3 to operation 2 resulted in the optimum network shown in Figure 5.2. Again, this design agrees with that presented by Doyle and Smith (1997). Network simplifications are usually explored by introducing specific constraints. Such simplifications are useful to examine the trade-off between complexity, flexibility and operability.

5.2.2 Example Two

The limiting process data for this example (Table 5.2) was presented by Doyle and Smith (1997). It consists of four water using operations and three contaminants. Mass loads of the contaminants are determined from the limiting freshwater flow rates and the limiting concentrations. The optimum network produced by the deterministic model is presented in Figure 5.3. The minimum freshwater target was found to be 81.22 tonnes/hr. Unfortunately, Doyle and Smith (1997) did not present the design of their optimum network for Example-2. However, they reported the minimum freshwater target as 95.73 tonnes/hr for their linear formulation and 81.22 tonnes/hr for the nonlinear formulation. As the GAMS run of the model indicated total fresh water requirement of 81.22 tonnes/hr which is identical to the value reported in the published paper, this shows the model is robust and reproduces the same results.

Table 5.2: Process limiting data for Example-2.

Operation	Contaminants	Limiting Freshwater (tonnes/hr)	C_{in}^{max} (ppm)	C_{out}^{max} (ppm)	Load (kg/hr)
1	a	34	0	160	5.44
	b		0	450	15.30
	c		0	30	1.02
2	a	75	200	300	7.50
	b		100	270	12.75
	c		500	740	18.00
3	a	20	600	1,240	12.80
	b		850	1,400	11.00
	c		390	1,580	23.80
4	a	80	300	800	40.00
	b		460	930	37.60
	c		400	900	40.00

For the design shown in Figure 5.3, direct water reuse is mainly from Operation 1 to Operations 3 and 4, and Operation 2 to Operation 4. There is no reuse from Operations 3 and 4.

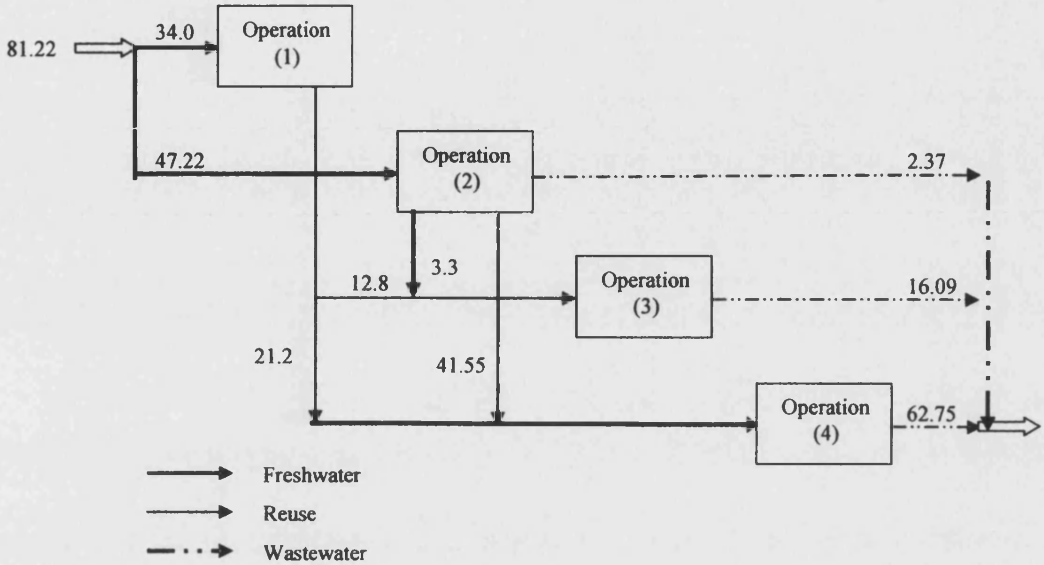


Figure 5.3: Optimum network for Example-2.

5.2.3 Example Three

Bagajewicz et al. (2000) presented a typical refinery wastewater network consisting of eight water-using processes. In their case study, four contaminants were considered. Limits on inlet and outlet concentrations of each pollutant were imposed a priori on every process, and fixed loads of contaminants were assumed. Process limiting data for this literature example is shown in Table 5.3.

Bagajewicz et al. (2000) used a cost objective function, which consisted of annualized capital cost and operating costs. The capital cost included the cost of piping and pumps, whilst the operating cost included freshwater and pumping costs. They introduced a tree searching methodology with efficient branch cutting criteria to solve globally the multi-component water allocation problem. Reported 'global' optimal results are shown in Table 5.4 and illustrated in Figure 5.4. Four 'sub-optimal' solutions were also reported. All reported networks demanded 162.59 tonnes/hr of freshwater with slight differences in water reuse and the total capital costs.

Table 5.3: Process limiting data for Example-3 (Bagajewicz et al., 2000).

Process	Contaminant	C_{in}^{max}, (ppm)	C_{out}^{max}, (ppm)	Load (kg/hr)
(1) Caustic Treating (CUT)	Salts	300	500	0.18
	Organics	50	500	1.20
	H_2S	5000	11000	0.75
	NH_3	1500	3000	0.10
(2) Distillation (DIS)	Salts	10	200	3.61
	Organics	1	4000	100.00
	H_2S	0	500	0.25
	NH_3	0	1000	0.80
(3) Amine Sweetening (ASU)	Salts	10	1000	0.60
	Organics	1	3500	30.00
	H_2S	0	2000	1.50
	NH_3	0	3500	1.00
(4) Sweetening (Merox I) (MX1)	Salts	100	400	2.00
	Organics	200	6000	60.00
	H_2S	50	2000	0.80
	NH_3	1000	3500	1.00
(5) Sweetening (Merox II) (MX2)	Salts	100	350	3.00
	Organics	200	6000	75.00
	H_2S	50	1800	1.90
	NH_3	1000	3500	2.10
(6) Hydrotreating (HTU)	Salts	85	350	3.80
	Organics	200	1800	45.00
	H_2S	300	6500	1.10
	NH_3	200	1000	2.00
(7) Desalter I (DES1)	Salts	1000	9500	120.00
	Organics	1000	6500	480.00
	H_2S	150	450	1.50
	NH_3	200	400	0.00
(8) Desalter II (DES2)	Salts	800	9500	140.00
	Organics	1200	6500	220.00
	H_2S	150	450	1.20
	NH_3	200	400	0.00

The deterministic model has been solved for the fixed mass loads and the concentration limits shown in Table 5.3. The resulted optimum wastewater network is shown in Table 5.5. It demands 160.67 tonnes/hr of freshwater and reuses 52.35 tonnes/hr. This optimal solution seems better than the solution reported by Bagajewicz et al. (2000). It saves 1.92 tonnes/hr of freshwater by allocating an additional 4.97 tonnes/hr for direct reuse.

However, the connections for reuse from one unit to another are not similar for both solutions.

Table 5.4: Optimal solution reported by Bagajewicz et al. (2000)

Process	Freshwater (tonnes/hr)	Wastewater (tonnes/hr)	Reuse from				Reuse (tonnes/hr)
			CUT	DIS	ASU	HTU	
CUT	2.40	–	–	–	–	–	–
DIS	25.00	13.59	–	–	–	–	–
ASU	8.57	–	–	–	–	–	–
MX1	9.76	10.35	–	–	0.59	–	0.59
MX2	12.19	12.93	–	–	0.74	–	0.74
HTU	25.00	–	–	–	–	–	–
DES1	50.76	84.20	2.40	–	6.04	25.0	33.44
DES2	28.91	41.52	–	11.41	1.20	–	12.61
Total	162.59	162.59	2.40	11.41	8.57	25.0	47.38

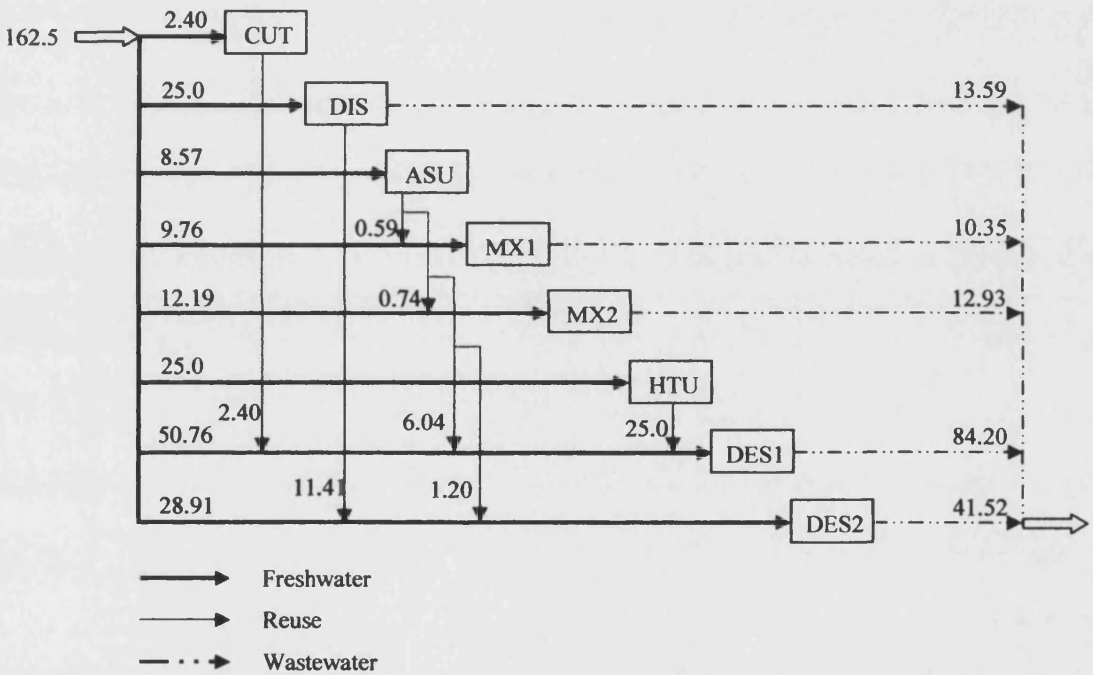


Figure 5.4: Optimum network for Example-3 as reported by Bagajewicz et al. (2000).

The optimal network solution reported in Table 5.5 has been obtained using the cost function for which the cost of direct reuse from one unit to another is fixed. However, the solution reported by Bagajewicz et al. (2000) accounted for total annualized capital and operating costs including costs of piping and pumping. For this reason, their optimal freshwater demand and reuse are different from our results. In an attempt to narrow the differences in connectivity, the cost of direct reuse has been simply assumed to be a function of the distances between the water-using units. Such variations in reuse costs were accounted for by multiplying the fixed reuse cost by $d \times 10^{-3}$, where d is the distance between the processes, listed in Table 5.6. Optimal network results obtained after considering the variations in reuse costs are listed in Table 5.7 and presented schematically in Figure 5.5. The resulting network is quite similar to that reported by Bagajewicz et al. (2000). It demands 160.67 tonnes/hr of freshwater and reuses 53.03 tonnes/hr. The difference in reuse is that wastewater is reused from the caustic treating unit (CUT) to the hydrotreater (HTU) rather than the first desalter (DES1), and the DES1 receives the reuse stream from the distillation unit (DIS) rather than amine sweetening unit (ASU).

Table 5.5: Optimal solution obtained without imposing constraints.

Process	Freshwater (tonnes/hr)	Wastewater (tonnes/hr)	Reuse from CUT	DIS	ASU	HTU	Reuse (tonnes/hr)
CUT	2.40	–	–	–	–	–	–
DIS	25.00	8.61	–	–	–	–	–
ASU	8.57	–	–	–	–	–	–
MX1	8.39	10.35	1.64	0.31	–	–	1.95
MX2	12.28	12.93	–	0.65	–	–	0.65
HTU	25.00	–	–	–	–	–	–
DES1	49.97	87.27	0.76	2.97	8.57	25.0	37.30
DES2	29.06	41.51	–	12.45	–	–	12.45
Total	160.67	160.67	2.40	16.38	8.57	25.0	52.35

Table 5.6: Distance (*d in ft*) between water-using processes (Bagajewicz et al., 2000)

To Process	From Process CUT	DIS	ASU	MX1	MX2	HTU	DES1
DIS	1200						
ASU	600	900					
MX1	900	900	1200				
MX2	1200	1200	1500	300			
HTU	600	1200	300	1500	1800		
DES1	900	900	600	1800	2100	300	
DES2	1200	600	300	1500	1800	600	300

Table 5.7: Optimal solution obtained after accounting for different reuse costs

Process	Freshwater (tonnes/hr)	Wastewater (tonnes/hr)	Reuse from				Reuse (tonnes/hr)
			CUT	DIS	ASU	HTU	
CUT	2.40	–	–	–	–	–	–
DIS	25.00	8.61	–	–	–	–	–
ASU	8.57	–	–	–	–	–	–
MX1	9.75	10.35	–	–	0.59	–	0.59
MX2	12.19	12.93	–	–	0.74	–	0.74
HTU	23.27	–	2.40	–	–	–	2.40
DES1	51.34	87.27	–	10.27	–	25.67	35.94
DES2	28.15	41.51	–	6.12	7.24	–	13.36
Total	160.67	160.67	2.40	16.39	8.57	25.67	53.03

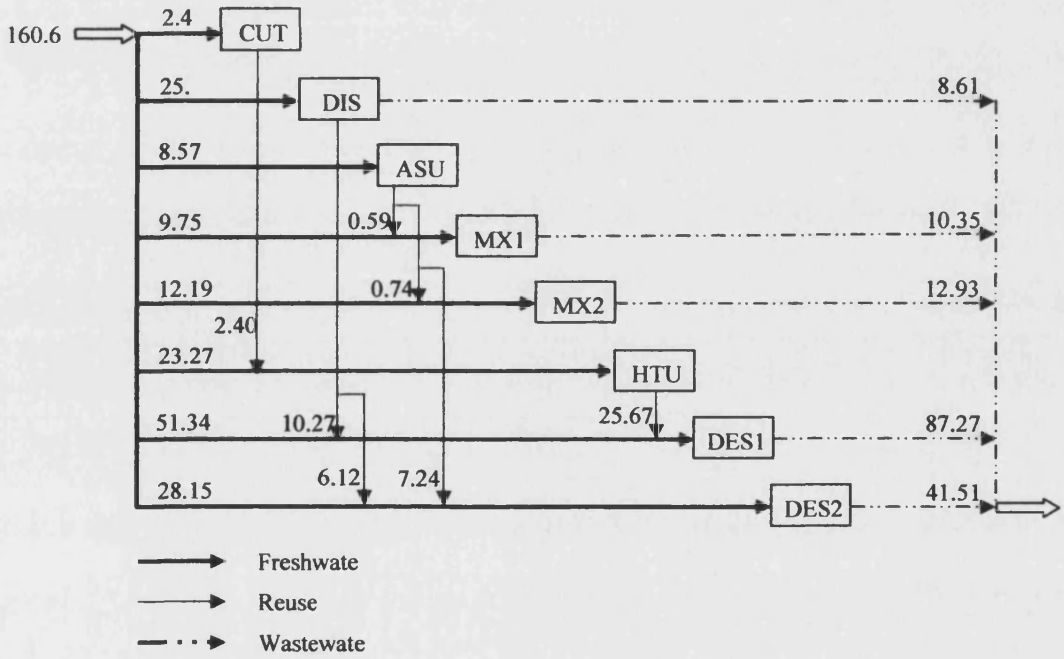


Figure 5.5: Optimum network for Example-3, accounting for different reuse costs.

5.2.4 Concluding Remarks

The results obtained from the three literature examples presented above provide an excellent validation for the optimization model proposed in this study. The optimum wastewater networks obtained are comparable with the results reported in the literature and in some cases slightly better in terms of freshwater demands and amounts of direct reuse. The third example demonstrated the flexibility of the mathematical formulation in accommodating further considerations. In this example, different reuse costs were assumed for different operations. Similar adjustments can be easily introduced due to the fact that the objective function is represented as a cost function rather than just minimizing the total demand of freshwater.

5.3 Refinery Wastewater Network – Base Case

The wastewater network of a typical 400,000 barrel per stream day oil refinery will be considered throughout this study to demonstrate the proposed wastewater minimization models and formulations. The network consists of nine major water- and/or steam-using operations. The unit operations include an atmospheric crude distillation unit (CDU), a vacuum distillation unit (VDU), a tail gas treatment unit (TGT), a hydro-cracker unit (HCR), a gas-oil desulphurization unit (GOD), an atmospheric residue desulphurization unit (ARD), a kerosene desulphurization unit (KD), a fluid catalytic cracking unit (FCC), and a desalting unit (DES).

Four contaminants are considered: ammonia (NH_3), chloride (Cl_2), hydrogen cyanide (HCN) and hydrogen sulphide (H_2S). NH_3 and H_2S exist in the wastewater streams from all operations, whilst the sources of Cl_2 and HCN are from the DES and FCC units respectively. Nominal water and steam demands of each unit, in addition to the concentration limits and contaminant concentrations, are listed in Table 5.8. These values have been derived from actual design and licensor data.

The case presented in Table 5.8 will be referred to as the base-case (*Case-0*) against which results of other case studies will be compared.. For this case, wastewater streams are neither reused nor regenerated-reused. The total freshwater demand amounts to 342.1 tonnes/hr, of which 143.6 tonnes/hr is supplied to the boiler for steam generation. Consequently, the amount of wastewater sent to the treatment and disposal plant is 342.1 tonnes/hr. The wastewater network for *Case-0 is* shown schematically in Figure 5.6.

Table 5.8: Nominal freshwater and steam demands and maximum allowable inlet & design outlet concentrations for the base case (*Case-0*)

Unit	Demand (tonnes/hr)		Max. allowable inlet conc. & design outlet conc (ppm)								Wastewater (tonnes/hr)
	Water	*Steam*	H_2S		NH_3		Cl_2		*HCN*		
BOILER	143.6		0	0	0	0	0	0	0	0	4.15
CDU	1.0	52.50	80	89	80	259	10	10	0	0	53.50
VDU		45.35	50	99	50	70	10	10	0	0	45.35
TGT		27.20	80	1514	200	1152	10	10	0	0	27.20
HCR	16.2	1.00	100	25700	200	12627	10	10	0	0	17.20
GOD	8.4	6.50	100	3331	100	884	10	10	0	0	14.90
ARD	68.4	0.50	50	41660	200	27158	10	10	0	0	68.90
KD	2.7	1.80	100	379	100	198	10	10	0	0	4.50
FCC	13.6	4.50	10	3000	100	300	10	40	0	100	18.10
DES	88.6	0.10	20	20	50	100	20	300	0	0	88.7
Total	342.1	139.45									342.1

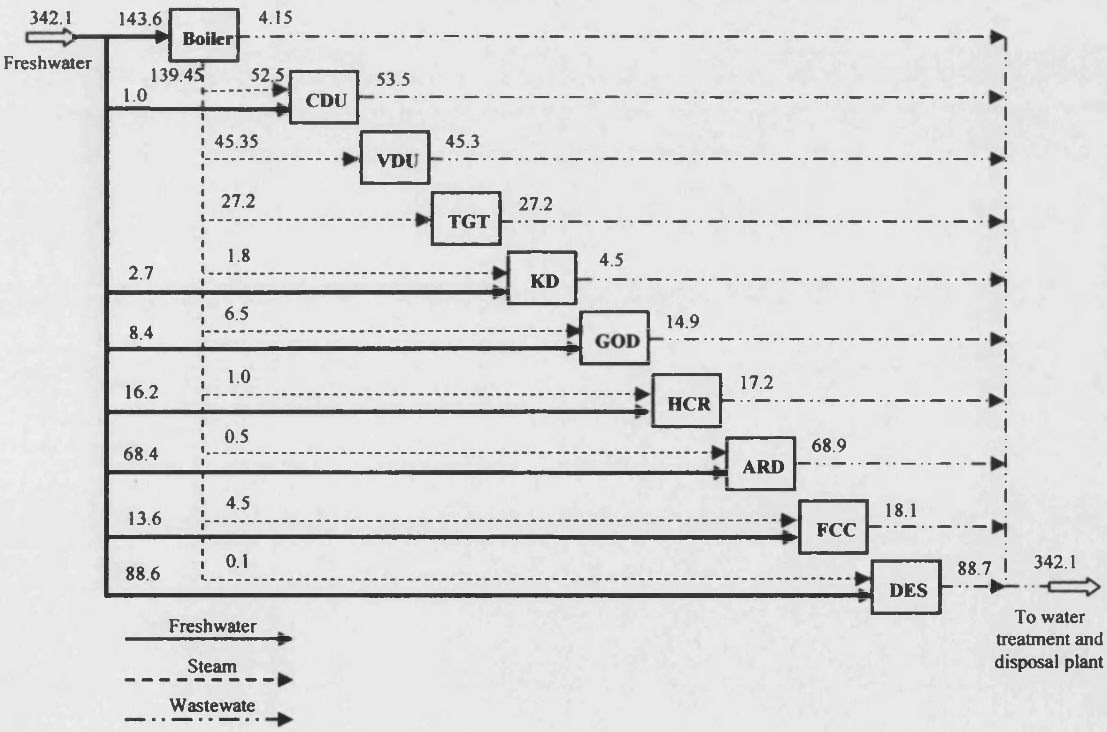


Figure 5.6: Wastewater network for the base case (*Case-0*)

The deterministic optimization model will be utilized to develop a number of wastewater minimization scenarios for the refinery network presented by *Case-0*. The cost function proposed in Chapter 4, Equation 4.7, is based on minimizing the total cost of the wastewater network. The cost factors which are used to estimate the freshwater cost, the cost of water reuse, regeneration and wastewater treatment and disposal are listed in Table 5.9.

Three wastewater minimization options will be considered by using the following three case studies:

***Case-1*:** **Direct-Reuse** – Wastewater from one unit is directly reused in another unit, without regeneration.

Case-2: **Regeneration-Reuse** – Wastewater from one unit is first regenerated then reused in other units.

Case-3: **Reuse & Regeneration-Reuse** – Wastewater from one unit is either directly reused in other units, or reused after partial regeneration (i.e. both reuse and regeneration-reuse options are considered).

Table 5.9: Cost of freshwater, reuse, regeneration and treatment.

Type of Water	**Cost in KD[1]/tonne**
Freshwater, C_{FW}	0.60
Regenerated Water, C_{RW}	0.10
Reuse Water, C_{RU}	0.05
Wastewater treatment and disposal, C_{WT}	1.00

[1] 1 KD = US$ 3.3

5.4 Case-1: Direct Reuse

This case considers reusing wastewater in process units without any treatment or partial regeneration. For example, knowing that the sour water generated from the VDU unit has very low concentrations of H_2S and NH_3 it can be used in another unit provided that contaminant levels of wastewater from the VDU are less than the maximum acceptable contaminant levels of the unit that will be receiving the wastewater as process water.

Optimization results for the direct reuse option are listed in Table 5.10 and shown schematically in Figure 5.7. The results show that reusable wastewater comes mainly from the fractionation units, CDU and VDU. Both units demand no freshwater and are considered as major steam consuming units in the refinery. All wastewater generated by condensing steam in the VDU unit has been reused in other units, while 60% of the CDU wastewater has been directly used in other units. The total amount of wastewater that has been directly reused is 78.08 tonnes/hr. The optimum wastewater network resulted in freshwater and wastewater flow rates of 264.37 tonnes/hr each (against the base case value of 342.1 tonnes/hr). The benefits are 22.7% reduction in freshwater demand, hence 22.7% reduction in wastewater generation.

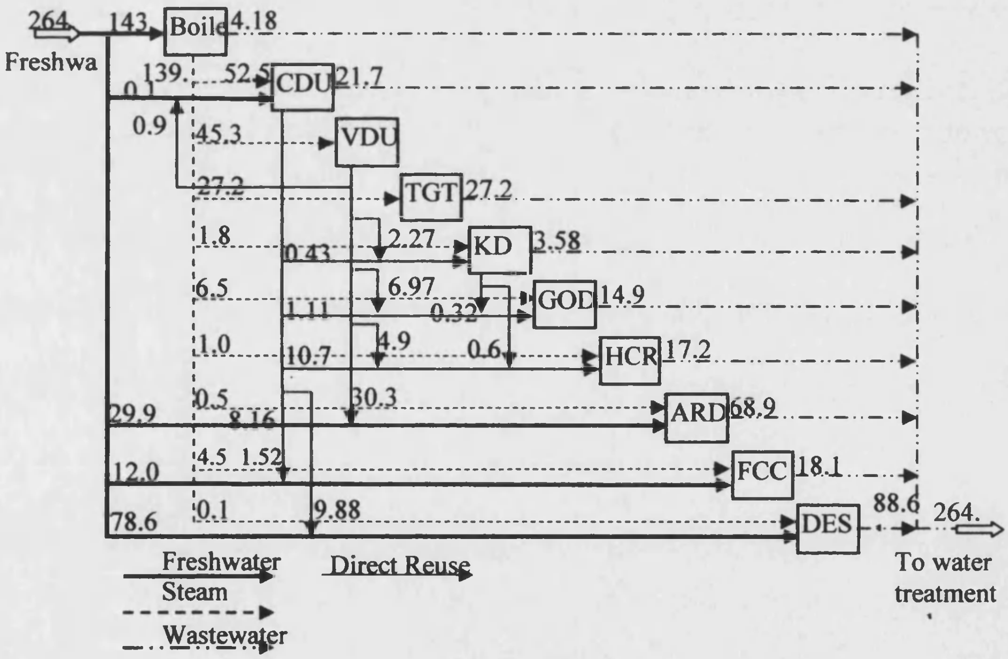


Figure 5.7: Wastewater network for direct water reuse option, (*Case-1*)

Table 5.10: Results of direct water reuse, (*Case-1*).

	Steam	Freshwater	Wastewater	Reuse From:			Total Reuse
	T/hr	*T/hr*	*To Treat.*	CDU	VDU	KD	
Boiler	–	143.63	4.18				
CDU	52.50	0.10	21.70		0.90		0.90
VDU	45.35	–	–				
TGT	27.20	–	27.2				
KD	1.80	–	3.58	0.43	2.27		2.70
GOD	6.50	–	14.90	1.11	6.97	0.32	8.40
HCR	1.00	–	17.20	10.71	4.90	0.6	16.21
ARD	0.50	29.93	68.90	8.16	30.31		38.47
FCC	4.50	12.08	18.10	1.52			1.52
DES	0.10	78.63	88.61	9.88			9.88
Total	139.45	264.37	264.37	31.81	45.35	0.92	78.08

The network generated for *Case-1* suggests that a considerable amount of freshwater consumption can be reduced by installing pipes to route the sour water from the CDU and VDU to other units.

5.5 Case 2: Regeneration

Wastewater generated by some operations can not be reused directly in other units due to high concentrations of impurities which are above the minimum allowable concentration limits of other units. For instance, wastewater from units like the HCR and ARD cannot be reused due to high concentrations of impurities. However, this wastewater can be reused after suitable regeneration. *Case-2* will consider the option of reusing wastewater after partial treatment. For example, knowing that the sour water generated from ARD/HCR/VDU units have very high concentrations of H_2S and NH_3, wastewater from these units is regenerated to reduce the contaminants and the treated water is then reused in other units provided that the concentration levels are less than the maximum acceptable levels for the unit that is receiving the treated water.

Only one regenerator has been considered for *Case-2*, and its capacity is limited to 165 tonnes/hr. It is further assumed that the regenerator removes only H_2S and NH_3 contaminants. The minimum allowable concentrations of H_2S, NH_3, Cl_2 and HCN of the regenerated wastewater are 10, 10, 10 and 0 ppm, respectively. Hence, no HCN is allowed into the regeneration unit.

Optimization results of the regeneration case are listed in Table 5.11 and shown schematically in Figure 5.8.

The optimum wastewater network indicates that the maximum capacity of the regenerator (165 tonnes/hr) has been utilized. Regenerated wastewater is reused by seven units, and major using units are the ARD and the desalter (DES). This resulted in freshwater and wastewater flow rates of 178.94 tonnes/hr, compared with 342.1 tonnes/hr for base case (*Case-0*). This means that the regeneration option provided 47.7% reduction in freshwater demand and wastewater flow to the treatment and disposal plant.

Table 5.11: Optimization results of Regeneration option, (*Case-2*).

	Steam	**Freshwater**	**Wastewater**		
	T/hr	***T/hr***	***To Regen.***	***To Treat.***	***From Regen.***
Boiler	–	143.63	–	4.18	–
CDU	52.50	–	–	53.50	1.0
VDU	45.35	–	36.8	8.55	–
TGT	27.20	–	27.2	–	–
KD	1.80	–	–	4.50	2.7
GOD	6.50	–	14.9	–	8.4
HCR	1.00	–	17.2	–	16.2
ARD	0.50	–	68.9	–	68.4
FCC	4.50	–	–	18.10	13.6
DES	0.10	35.31	–	90.11	54.7
Total	139.45	178.94	165.0	178.94	165.0

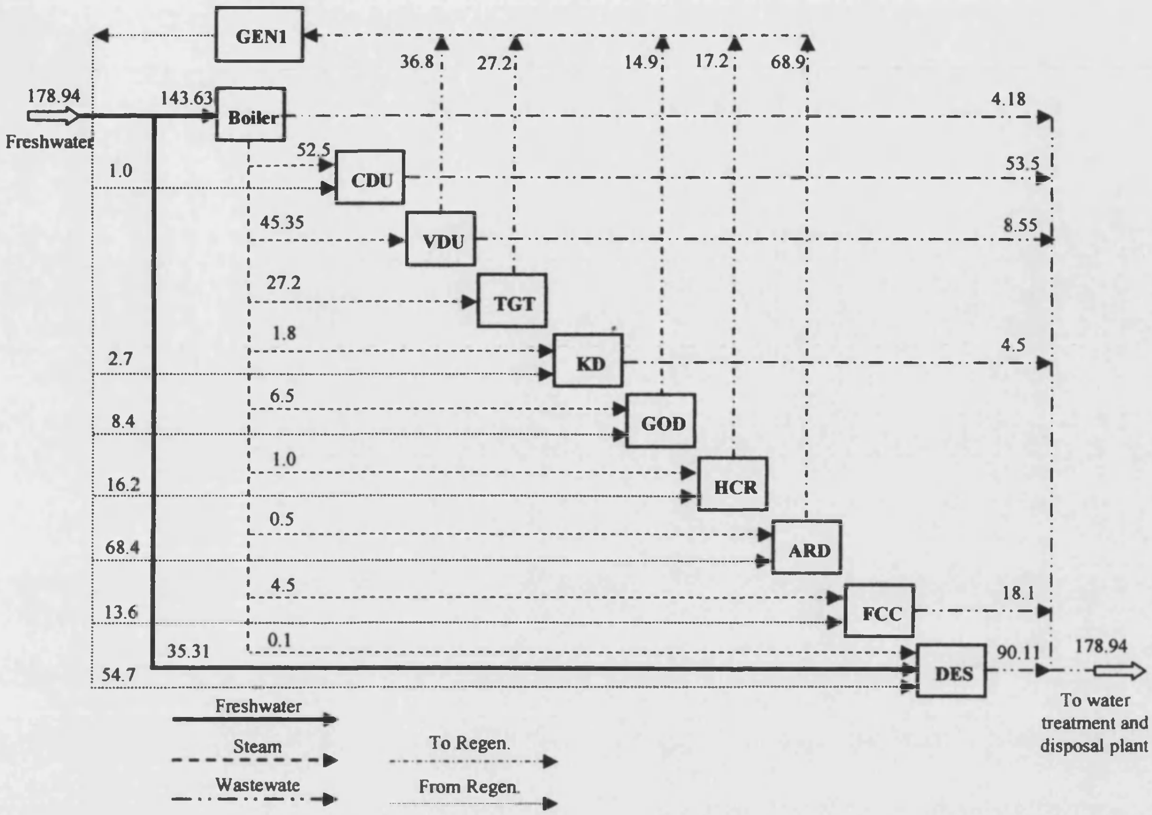


Figure 5.8: Flow sheet of water using units Wastewater network for water Regeneration option, (*Case-2*).

Apart from the condensing steam, the optimum wastewater network for *Case-2* shows that freshwater is demanded by the desalter only. In addition, four operations (TGT, GOD, HCR and ARD) recycle all generated wastewater back to the regenerator. Furthermore, the ARD operation, which directly reused the highest amount in *Case-1*, is also a major user of regenerated water (41% of total regenerated amount). Another important observation is that the fractionation units, which were the main contributors of the direct reuse wastewater quantities (*Case-1*), played a minor role in the regeneration-reuse option. Even though the VDU unit sends 81% of the produced wastewater to the regeneration unit, regenerated water is not consumed by this unit. On the other hand, the CDU unit routes all produced wastewater to the treatment and disposal plant.

The above discussion indicates that allowing both direct reuse and regeneration-reuse options may act positively in further reduction in the amount of freshwater demands, hence in the amounts of wastewater produced.

5.6 Case-3: Direct Reuse & Regeneration

The two case studies discussed above (*Case-1* and *Case-2*) indicated that further reduction in wastewater production may be achieved by combining direct reuse with regeneration-reuse. For the direct reuse option (*Case-1*), wastewater has been mainly reused from the CDU and VDU operations. By combining regeneration-reuse, wastewater from units like the HCR and ARD may be also utilized.

Case-3 investigates the option of allowing wastewater to be either directly used by other operations, or reused after regeneration. Similar to Case-2, one re-generator is used with a capacity of 165 tonnes/hr with the capability of removing H_2S and NH_3. The GAMS file for this case is included in Appendix B.

The Optimization results suggesting the optimum wastewater network for *Case-3* are summarized in Table 5.12 and shown schematically in Figure 5.9. The results show that freshwater is used just for steam generation (143.63 tonnes/hr). This means that *Case-3* provided 58% reduction in freshwater demand and wastewater flow to the treatment and disposal plant. Such a reduction is the maximum that may be achieved due to the fact that it is not feasible to reuse wastewater as boiler feed water. The purity required by boiler feed water is one of the most stringent in the refinery. Even though it is technically possible to treat wastewater generated from refinery units to achieve the level of purity required for boiler feed water, it is not economically feasible. The operating cost for such regeneration and treatment plant will be high compared to the cost of fresh water.

Table 5.12: Optimization results of Direct Reuse & Regeneration option, (*Case-3*).

	Steam	Freshwater	Wastewater			Reuse from		
	T/hr	*T/hr*	*To Regen.*	*To Treat.*	*From Regen.*	CDU	VDU	KD
Boiler	–	143.63	–	4.18	–	–	–	–
CDU	52.50	–	36.15	0.73	0.11	–	0.89	–
VDU	45.35	–	–	–	–	–	–	–
TGT	27.20	–	27.20	–	–	–	–	–
KD	1.80	–	2.85	0.73	–	0.43	2.27	–
GOD	6.50	–	14.17	0.73	–	1.11	6.97	0.32
HCR	1.00	–	16.47	0.73	–	10.71	4.90	0.60
ARD	0.50	–	68.17	0.73	33.70	4.38	30.32	–
FCC	4.50	–	–	18.10	13.60	–	–	–
DES	0.10	–	–	91.32	91.22	–	–	–
GEN1	–	–	–	26.37	–	–	–	–
Total	139.45	143.63	165.0	143.62	138.63	16.63	45.35	0.92

All processes reuse wastewater directly from other processes or from the regenerator. Again, as for *Case-1*, wastewater is directly reused from the fractionation units, CDU and VDU. Wastewater is directly used mainly in KD, GOD, HCR and ARD operations. The total amount which is directly reused by different processes is 62.9 tonnes/hr. Maximum capacity of the regeneration unit has been utilized. The regenerator receives 165 tonnes/hr and recycles back 138.63 tonnes/hr for reuse, whilst the rest (26.37 tonnes/hr) is routed to the treatment and disposal plant. Regenerated wastewater is mainly reused by the ARD, FCC and DES operations. The value of the cost function for *Case-3* is 1.136 MM KD/year.

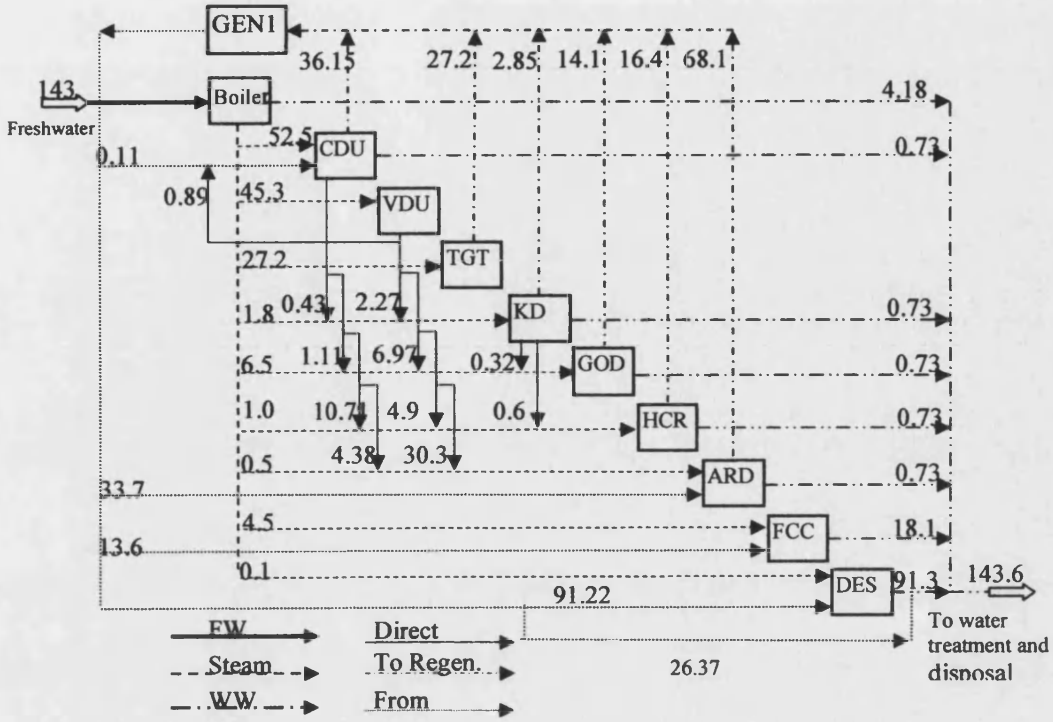


Figure 5.9: Wastewater network for water Direct Reuse & Regeneration option, (*Case-3*).

The optimum network results reported in Table 5.12 show that only 0.89 tonnes/hr is directly reused from the VDU to the CDU. It shows also that minor quantities are directly reused from the KD to the GOD and HCR. These quantities may be satisfied by means other than direct reuse, hence, reducing unnecessary piping and instrumentation costs. In order to make the optimal wastewater network more practical and realistic to implement, Case-3 has been refined by introducing constraints on the direct reuse from the VDU to the CDU and from the KD to the GOD and HCR. Results of the refined network are listed in Table 5.13. The refined network is quite similar to the original one. Freshwater is again demanded for steam generation only, and maximum capacity of the regenerator is utilized. However, the refined network is more realistic concerning the quantities routed to the regenerator. In addition, direct reuse quantities are provided by the two fractionation units, CDU and VDU.

The penalty paid in refining the optimal wastewater network of Case-3 is reducing the amount of direct reuse by 0.89 tonnes/hr (from 62.90 to 62.01 tonnes/hr). Nevertheless, the value of the cost function has increased by only 0.6% (from 1.136 to 1.142 MM KD/year).

The network of *Case-3* will be used as a reference when studying the impact of uncertainty on the optimal wastewater network of the refinery. The resulting value of the cost function is 1.136 MM KD/year.

Table 5.13: Refined network for Direct Reuse & Regeneration-Reuse option, (*Case-3*).

	Steam	Freshwater	Wastewater			Reuse from	
	T/hr	*T/hr*	*To Regen.*	*To Treat.*	*From Regen.*	CDU	VDU
Boiler	–	143.63	–	4.18	–	–	–
CDU	52.50	–	32.3	4.54	1.00	–	–
VDU	45.35	–	–	–	–	–	–
TGT	27.20	–	27.2	–	–	–	–
KD	1.80	–	4.5	–	–	0.43	2.27
GOD	6.50	–	14.9	–	–	1.33	7.07
HCR	1.00	–	17.2	–	–	11.11	5.09
ARD	0.50	–	68.9	–	33.69	3.79	30.92
FCC	4.50	–	–	18.10	13.60	–	–
DES	0.10	–	–	91.32	91.22	–	–
GEN1	–	–	–	25.49	–	–	–
Total	139.45	143.63	165.0	143.63	139.51	16.66	45.35

5.7 Conclusions

The main objective of the current Chapter was to test and validate the deterministic mathematical optimization model proposed in Chapter 4. The deterministic optimization model was first applied to three examples reported in the literature. The resulting wastewater networks were found to be consistent with those reported in the literature. The capabilities of the proposed model were further demonstrated through the flexibility by which additional considerations may be introduced. The third example considered the case where direct reuse costs are a function of the physical distances between different operations.

A number of wastewater network examples may be found in the literature. Unfortunately, most of these networks are hypothetical and do not reflect actual operational practices in terms of the contaminants involved and their loads. A wastewater network of a typical refinery consisting of nine water-using operations has been introduced in this Chapter. The outlined network includes all major water-using units in actual refinery operation, and forms a prototype for testing the techniques proposed in this work. A remarkable characteristic feature of the proposed network is the consideration of condensing steam as a source of wastewater. Most refinery processes use direct contact steam for stripping light components. The quantities of wastewater produced from condensing steam are significant and should not be ignored.

The base case (*Case-0*) demands 342.1 tonnes/hr of freshwater. Three wastewater minimization options have been considered. The total freshwater requirement for all water-using units including the boilers can be reduced by 22.7%, if part of the sour water generated from various process units is directly reused in other process units (*Case-1*). Fresh water can be reduced to 47.7% compared to base case, by treating the sour water in a regenerator and recycling it to the process units (*Case-2*). The fresh water requirement can be further reduced to about 58% compared to base case by combining the above two techniques, viz., reuse and regeneration-reuse (*Case-3*). The optimum network for *Case-3* demands freshwater for steam generation only. All operations are satisfied by direct reuse or regeneration-reuse. Further reduction in the amount of wastewater production is not possible because it is not feasible to reuse generated wastewater as boiler feed water.

The examples and case studies discussed in this Chapter have demonstrated the effectiveness of the proposed mathematical model in solving wastewater minimization problems. The problem that we will try to investigate now is whether the optimum wastewater networks developed in this Chapter are resilient to variations in operating conditions. This involves studying the nature of existing uncertainties, and their impact on the optimum network. These issues will be discussed in the next Chapter.

Chapter Six

6. UNCERTAINTIES IN WASTEWATER NETWORKS

6.1. Introduction

Maintaining product specifications is the primary goal in operating process plants. To do so, operating conditions are changed frequently. Moreover, in some instances, operation is switched from one mode to another to meet market demands of specific products. It is therefore apparent that operation of process plants is usually not steady and regular. Such operational changes introduce deviations and uncertainties in a number of parameters.

Accordingly, operational uncertainties are expected to have a direct effect on the proposed optimum wastewater networks. In designing these networks, two main assumptions are usually made (Bagajewicz, 2000):

- Constant pollutant load is picked up in each process.
- Maximum inlet and outlet concentrations in each process are fixed.

It is obvious that operational uncertainties may affect both the pollutant load as well as the limiting concentration of pollutants. For instance, deviations in operating temperature have a direct effect on solubility, hence, on the mass load of pollutants. This is equally true for deviations in throughputs, feedstock quality and product quality specification.

In order to build a wastewater network that can be practically implemented and reliable, it is important that this network is resilient to operational uncertainties. The main objective of the current chapter is to study the impact of uncertainties on the optimum wastewater network structures. This will be achieved through a number of sensitivity analysis scenarios on the developed optimum wastewater networks. The deterministic mathematical model tested in Chapter 5 will be utilized in carrying out the sensitivity analysis. All the literature examples in Chapter 5 considered reuse only. In order to test the sensitivity of the wastewater network, one more example with a regenerator will be considered in this chapter.

The case studies that will be considered here are the four literature examples in addition to the refinery case study presented in the previous chapter. Two types of uncertainty will be addressed. For the first one, uncertainty will be introduced directly as deviations in mass loads. For the second one, uncertainty will be introduced in operating conditions. Hence, deviations in mass loads are indirect. The chapter starts by discussing uncertainties in mass loads. This is followed by identifying the sources of operational uncertainties and how these uncertainties are quantified. Operational uncertainties will be then applied to the refinery case study to determine its sensitivity to changes in key operating variables.

6.2. Sensitivity Analysis of Literature Examples

Three literature examples have been studied in the previous chapter. All three examples involved multiple contaminants. The first and second examples consisted of three and four water-using operations and were adopted from Wang and Smith (1994) and Doyle and Smith (1997), respectively. The third example had eight operations and was adopted from Bagajewicz et al. (2000). Only direct wastewater reuse was allowed and no regeneration units were considered. Optimization results demonstrated the capabilities of the proposed deterministic mathematical model in generating optimal wastewater networks.

Before studying the sensitivity of the refinery-scale case study which was introduced in the previous chapter and involves deviations in key operating conditions, it is worth considering the sensitivity of the literature examples. Uncertainty is assumed here in the mass loads of the contaminants. Optimum wastewater networks generated for the process limiting concentrations and mass loads listed in Tables 5.1, 5.2 and 5.3 will be considered here as the base cases against which results of the deviated cases are compared. The network structures of these base cases are shown in Figures 5.2, 5.3 and 5.5 respectively.

Sensitivity of the wastewater networks to deviations in mass loads was determined by assuming positive and negative changes in the fixed mass loads listed in Tables 5.1, 5.2 and 5.3. Two approaches were attempted in this investigation:

a) Determining the freshwater demands and reuse amounts for the fixed wastewater network topologies of the base cases for each change in mass load.

b) Determining new optimum wastewater network for each deviation in mass load.

The first approach is an operational problem. It assumes that the wastewater networks which were obtained for the base cases have already been implemented, and it is required to evaluate the changes in flow rates resulting from deviations in mass loads. For these cases, the deterministic optimization model was solved after forbidding direct reuse connections between process units that are not present in the networks of the base cases. On the other hand, the second approach can be considered as a design problem where new wastewater networks are constructed for the new mass loads. In this case, the deterministic model was solved without additional constraints. As a result, new network topologies (different from the base cases) may be obtained.

Optimum wastewater network results are found to be identical for both operational and design problems. Such results are interesting and give an indication that the networks might not be sensitive to changes in mass loads. Detailed results for the deviations in mass loads are presented in Tables 6.1, 6.2 and 6.3 for Examples 1, 2 and 3, respectively. Changes in the value of cost function, total freshwater demand and direct water reuse are also shown graphically in Figures 6.1, 6.2 and 6.3 respectively. Fresh Water, Unit Operations 1,2,3 are depicted as FW, OP(1), OP(2), OP(3) in Table 6.1

Table 6.1: Wastewater network results for deviations in mass loads, Example-1.

	Deviations in mass loads						
	– 20%	– 10%	– 5%	Base	+ 5%	+ 10%	+ 20%
Cost (MMKD/yr)	1.194	1.344	1.419	1.493	1.568	1.643	1.792
% Cost	– 20%	– 10%	– 5%	0%	+ 5%	+ 10%	+ 20%
Freshwater Demand (T/hr)	84.53	95.10	100.38	105.66	110.95	116.23	126.80
% FW	– 20%	– 10%	– 5%	0%	+ 5%	+ 10%	+ 20%
OP(1)	36.00	40.5	42.75	45.00	47.25	49.50	54.00
OP(2)	6.80	7.65	8.08	8.50	8.93	9.35	10.20
OP(3)	41.73	46.95	49.55	52.16	54.77	57.38	62.60
Reuse (T/hr)	22.54	25.35	26.76	28.17	29.58	30.99	33.80
% Reuse	– 20%	– 10%	– 5%	0%	+ 5%	+ 10%	+ 20%
OP(1) to OP(2)	20.40	22.95	24.23	25.50	26.78	28.05	30.60
OP(1) to OP(3)	2.14	2.40	2.53	2.67	2.80	2.94	3.20

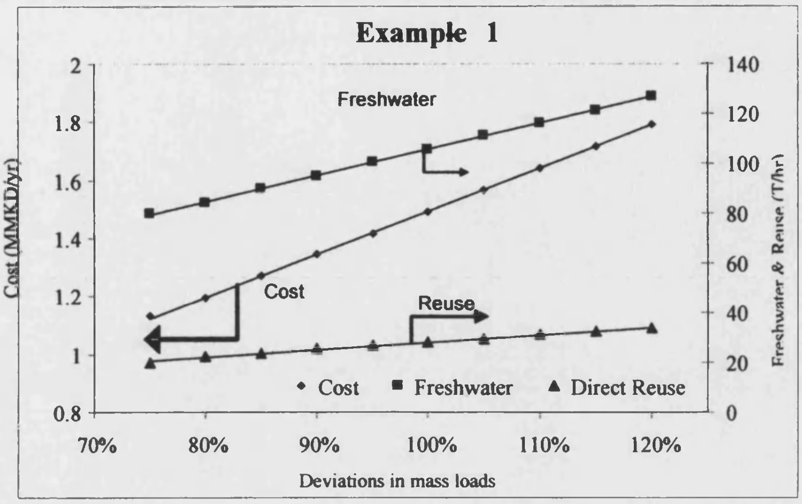


Figure 6.1: Changes in cost, freshwater demand and direct reuse for deviations in mass loads, Example-1

Sensitivity analysis results of the literature examples reveal the fact that network designs (topology) obtained for the base case may be fixed. This means that reuse connections between units are not affected by deviations in mass loads of contaminants. However, the amounts of freshwater demands and direct reuse are directly affected by these deviations. We can thus conclude that the wastewater network designs for the three examples are robust to changes in mass loads, and that only operational variations are expected.

Table 6.2: Wastewater network results for deviations in mass loads, Example-2.

	Deviations in mass loads						
	– 20%	– 10%	– 5%	Base	+ 5%	+ 10%	+ 20%
Cost (MMKD/yr)	0.9659	1.0867	1.1471	1.207	1.2678	1.328	1.448
% Cost	– 19.98%	– 9.97%	–4.96%	0.0%	+5.04%	+ 10.02%	+ 19.97%
Freshwater Demand (T/hr)	64.978	73.10	77.16	81.22	85.283	89.345	97.47
% FW	– 20.00%	–10.00%	–5.0%	0.0%	+ 5.0%	+10.00%	+ 20.01%
OP(1)	27.20	30.60	32.30	34.34	35.70	37.40	40.80
OP(2)	37.78	42.50	44.86	47.69	49.58	51.94	56.67
Reuse (T/hr)	63.082	70.967	74.91	78.853	82.795	86.738	94.623
% Reuse	– 20.0%	– 10.0%	–5.0%	0.0%	+ 5.0%	+ 10.0%	+ 20.0%
OP(1) to OP(3)	10.243	11.524	12.164	12.804	13.44	14.084	15.365
OP(1) to OP(4)	16.957	19.076	20.136	21.196	22.256	23.316	25.435
OP(2) to OP(3)	2.639	2.968	3.133	3.298	3.463	3.628	3.958
OP(2) to OP(4)	27.28	31.36	33.40	35.84	37.47	39.51	43.58

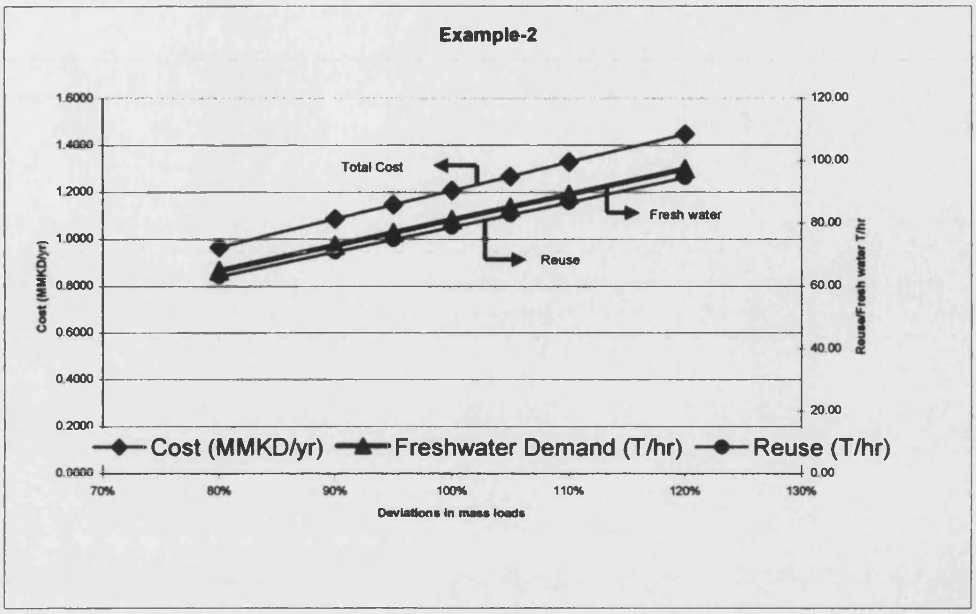


Figure 6.2: Changes in cost, freshwater demand and direct reuse for deviations in mass loads, Example-2

An interesting observation is that changes in costs, freshwater demands and reuse are directly proportional to changes in mass loads. This is clearly illustrated in Figures 6.1, 6.2 and 6.3. Hence, additional amounts of contaminants are washed out by using more freshwater in addition to increasing the amounts of direct reuse between water-using units. However, the rate of change of freshwater demands and reuse amounts are not the same for the three designs. In all cases, freshwater demand changed at higher rates. For Example-1, the rates of increase in freshwater and reuse amounts are 1.05 and 0.29 tonnes/hr per 1% increase in mass load of contaminants, respectively. This means that freshwater demands increase roughly three times the increase in direct reuse utilization. On the other hand, the network for Example-2 showed closer deviation rates in freshwater and reuse amounts (0.81 and 0.78 tonnes/hr per 1% deviation in mass load), whilst for Example-3, the rate of change in freshwater demands is again about three times the rate of change in reuse amounts (1.61 and 0.53 tonnes/hr per 1% deviation in mass load).

Table 6.3: Wastewater network results for deviations in mass loads, Example-3.

	Deviations in mass loads						
	– 20%	– 10%	– 5%	Base	+ 5%	+ 10%	+ 20%
Cost (MMKD/yr)	1.820	2.047	2.161	2.275	2.388	2.502	2.730
% Cost	– 20.0%	– 10.0%	– 5.0%	0.0%	+ 5.0%	+ 10.0%	+ 20.0%
Freshwater Demand (T/hr)	128.54	144.61	152.64	160.67	168.71	176.74	192.81
% FW	– 20.0%	– 10.0%	– 5.0%	0.0%	+ 5.0%	+ 10.0%	+ 20.0%
CUT	1.92	2.16	2.28	2.40	2.52	2.64	2.88
DIS	20.00	22.50	23.75	25.00	26.25	27.50	30.00
ASU	6.86	7.71	8.14	8.57	9.00	9.43	10.29
MX1	7.80	8.78	9.27	9.75	10.24	10.73	11.70
MX2	9.75	10.97	11.58	12.19	12.80	13.41	14.63
HTU	18.61	20.94	22.10	23.27	24.43	25.59	27.92
DES1	41.07	46.20	48.77	51.34	53.91	56.47	61.61
DES2	22.52	25.34	26.74	28.15	29.56	30.97	33.78
Reuse (T/hr)	42.42	47.72	50.37	53.02	55.67	58.33	63.63
% Reuse	– 20.0%	– 10.0%	– 5.0%	0.0%	+ 5.0%	+ 10.0%	+ 20.0%
CUT to HTU	1.92	2.16	2.28	2.40	2.52	2.64	2.88
DIS to DES1	8.22	9.24	9.76	10.27	10.78	11.30	12.32
DIS to DES2	4.89	5.51	5.81	6.12	6.42	6.73	7.34
ASU to MX1	0.47	0.53	0.56	0.59	0.62	0.65	0.71
ASU to MX2	0.59	0.67	0.70	0.74	0.78	0.81	0.89
ASU to DES2	5.79	6.52	6.88	7.24	7.60	7.97	8.69
HTU to DES2	20.53	23.10	24.38	25.67	26.95	28.23	30.80

As a conclusion, we can safely state that the optimal wastewater designs for the three literature examples are resilient to uncertainties in mass loads and variations in mass loads are compensated by modifying the amounts of freshwater needed. In fact, for the three problems discussed above, even a stochastic optimization approach would result in the same network structures and linear dependence on freshwater demands. However, this conclusion cannot be generalized to cover wastewater networks representing actual industrial practices due to the fact that the three examples can only be considered as hypothetical cases lacking a number of important issues. These include:

- Only direct reuse has been considered. Regeneration - reuse option is not considered.
- All wastewater streams are sent to the treatment and disposal plant with no limits or constraints on the type and amount of contaminants.
- No hydraulic limits have been considered, i.e., maximum water flow rate to most of the units cannot be increased beyond 110% of design because line size and capacity of pumps are only designed with 10% margins. For example, water flow rate to the desalter cannot be increased beyond 96 tonnes/hr as the control valve supplying water to the desalter will open fully because of its design.
- Uncertainty in mass loads was assumed to be the same for all contaminants. This might not be the case. Ammonia load may not change in the same ratio as that of hydrogen sulphide (this is true for almost all Hydro Desulphuriser units). Especially, Hydrogen Cyanide and Chloride do not have any relation with other contaminants like ammonia and hydrogen sulphide. In some cases, mass loads of certain contaminants might double, especially those with low concentrations.

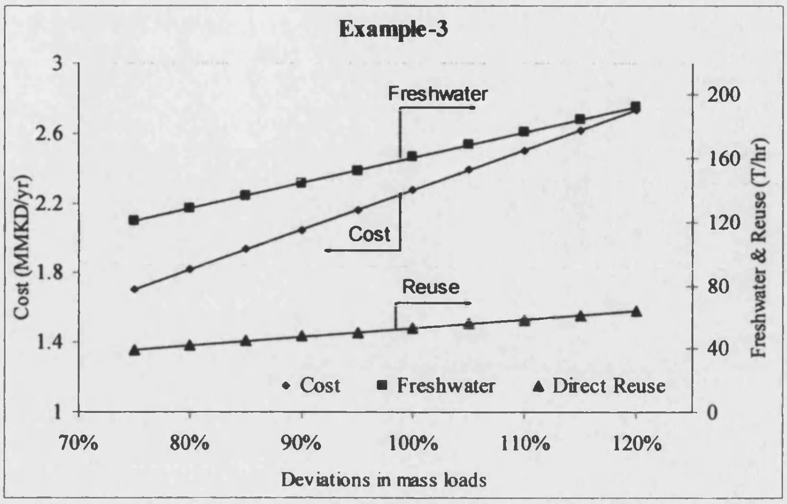


Figure 6.3: Changes in cost, freshwater demand and direct reuse for deviations in mass loads, Example-3

The three literature examples introduced in the previous chapter and discussed above provide an excellent means for testing the performance of the deterministic optimization models. The sensitivity analysis carried out in this section introduces the concept of uncertainty in wastewater networks and lays the ground for further considerations. All the three examples are consuming fresh water proportional to an increase in mass load of contaminants. Sensitivity of the wastewater network with a regenerator to deviations in mass loads will now be considered.

6.3. Sensitivity Analysis of Literature Example - 4 (with regenerator)

In all the three above cases, the fresh water consumptions are proportional to changes in mass load of contaminants. All these cases reused the water and no regenerator was considered and hence, this may be one of the main reasons for getting proportionality in fresh water requirements. Therefore one more example (Example-4) with a regenerator is now considered. This example consists of three water-using operations with a regenerator and is adopted from Wang and Smith (1994). The following units are considered in the example.

Steam Stripper (SS) of Crude Distillation Unit

Hydro Desulphuriser (HDS)

Desalter (DES)

Table 6.4: Wastewater network results for deviations in mass loads, Example-4

	Deviations in mass loads						
	– 20%	– 10%	– 5%	Base	5%	10%	20%
Cost (MMKD/yr)	0.6821	0.7455	0.7855	0.8254	0.8666	0.9396	1.089
% Cost	-17.0%	-10.0%	-5.0%	0.0%	5.0%	14.0%	32.0%
Freshwater Demand (T/hr)	45.11	49.35	52.09	54.83	57.57	62.73	73.3
% FW	-18.0%	-10.0%	-5.0%	0.0%	5.0%	14.0%	34.0%
SS	45	45	45	45	45	45	45
HDS	0.01	0.01	0.01	6.243	8.925	9.35	0.01
DES	0.1	4.338	7.079	3.588	1.397	3.879	19.285
Reuse (T/hr)	28.17	28.17	28.17	28.17	29.58	30.99	33.8
% Reuse	0.0%	0.0%	0.0%	0.0%	5.0%	10.0%	20.0%
SS TO HDS	25.5	25.5	25.5	25.5	26.78	28.05	30.6
SS TO DES	2.668	2.668	2.668	2.668	2.802	2.935	3.202
Regen (T/hr)	42.79	47.43	49.13	50.83	53.37	53.5	53.5
% Regen	-16.0%	-7.0%	-3.0%	0.0%	5.0%	5.0%	5.0%

In this study 53.5 tonnes/hr regenerator is considered which is same as that of the literature example (Wang and Smith, Waste water minimisation Fig 30 CES 1994). Results shown in Table 6.4 indicate that reuse can be increased to 28.2 tonnes/hr compared with the literature figure of 25.5 tonnes/hr. The difference may be due to regenerator specification for which complete data was not available in the literature. This reduces the regenerator requirement from 53.5 tonnes/hr as per literature to 50.8 for 100% mass load.

From Fig 6.4, it can be inferred that the model is very sensitive to any changes in mass load beyond 100% but almost not sensitive to reduction in mass load. This is mainly due to the presence of the regenerator which can treat about 53.5 tonnes/hr of water and fully utilized at around 105% mass load for this model.

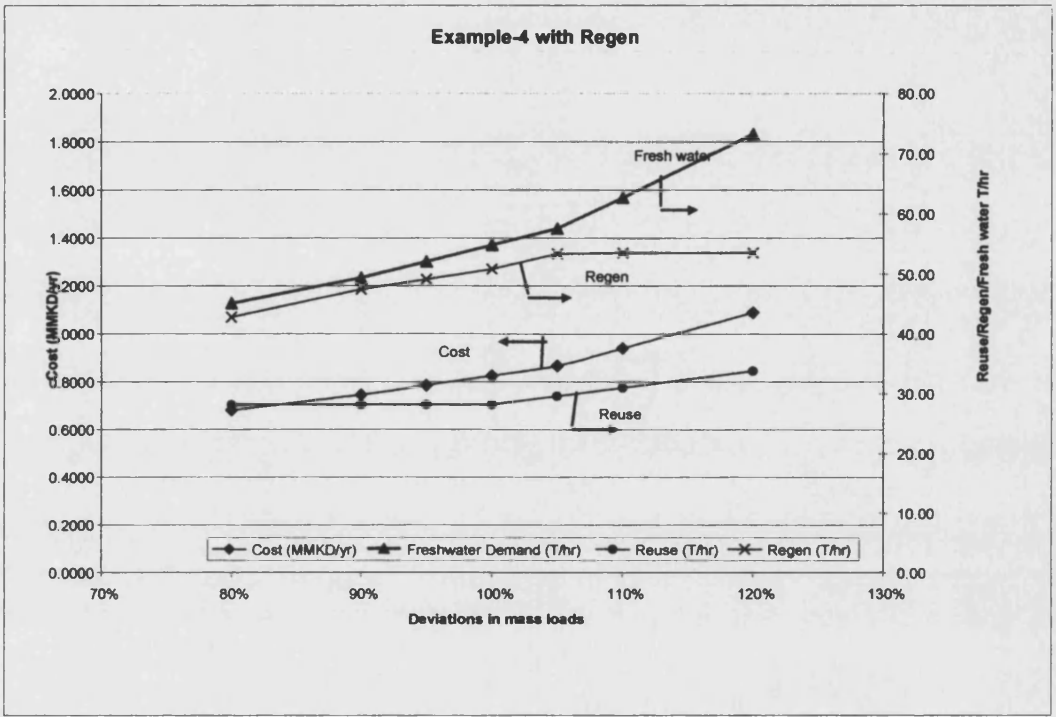


Figure 6.4: Changes in cost, freshwater demand and direct reuse for deviations in mass loads, Example- 4

Sensitivity analysis results of the literature example with the regenerator reveal the fact that network designs (topology) obtained for the base case may be fixed. This means that reuse connections between units are not affected by deviations in mass loads of contaminants. However, when the mass load increases by 20%, the amount of freshwater demand changes by 34% and reuse water increases only by 20%. Alternatively, when the mass load decreases by 20%, reuse water remains constant. This shows a non linear behaviour for the network. Hence there exists scope for optimisation under uncertain operating conditions.

From the above four examples we can safely state that the optimal wastewater designs for these examples are resilient to uncertainties in mass loads and variations in mass loads are compensated for by modifying the amounts of freshwater needed. For first three examples, reuse, fresh water and cost is changing proportionally to changes in the mass load. However for the fourth example reuse, fresh water, regenerated water and cost are changing disproportionately to the changes in mass load.

6.4. Sensitivity Analysis of Deterministic model with mass load changes

All the above models are based on mass load changes. It is now necessary to test our deterministic model in Chapter 5 (Case-3) for sensitivity on mass load changes. Based on plant data, it was found that the maximum expected mass load change is about ±5% and not ± 20% as we considered for the literature examples illustrated in sections 6.2 and 6.3. Therefore this case is now restricted to the 5% range.

Table 6.5: Sensitivity analysis results for deterministic model with mass load changes

	Deviations in mass loads		
	– 5%	Base	5%
Cost (MMKD/yr)	1.112	1.139	1.325
% Cost	-2.0%	0.0%	16.0%
Freshwater Demand (T/hr)	143.63	144.49	169.15
% FW	-1.0%	0.0%	17.0%
Reuse (T/hr)	83.64	86.769	88.507
% Reuse	-4.0%	0.0%	2.0%
Regen (T/hr)	162.6	165.0	165.0
% Regen	-1.0%	0.0%	0.0%

It can be observed from Table 6.5 that the fresh water requirement is more or less static at around 144 tonnes/hr for any mass load change on the lower side. However the freshwater requirement increases considerably on the higher side. This is in line with results of example-4. Therefore it is concluded that model considered in this thesis is resilient to various changes and hence is robust.

All the above cases are based on fixed mass loads, mainly because of the assumption that mass load changes are considered as fixed percentages such as 20%, 10% and 5%. These cases are hypothetical because in actual plant operation, outlet concentration changes based on temperature and total water to each unit cannot be changed due to process limitations. A significant variable used in the fixed mass load model is that the outlet concentration can be reduced by supplying more fresh water to a unit. This is not true for all unit operations. For example, any increase in water rate will absorb more hydrogen sulphide and ammonia from process streams. Hydrogen sulphide and ammonia concentration considered are primarily functions of operating pressure and temperature.

Therefore, the sensitivity of the refinery-wide waste water network to changes in key operating variables will be investigated in the next section.

6.5. Operational Uncertainties

Based on the above conclusions, the main source of uncertainty that will be considered in this thesis is variations in operating conditions. A direct consequence of variations in operating conditions is changes in the amounts (loads) of contaminants in different process units. Hence, variations arise in the concentrations and flow rates of wastewater streams. Factors contributing to uncertainties in operating conditions include variations in operating temperatures and pressures, throughputs and yields, operating modes and the quality of both feedstock and product slates. For illustrative purposes in the current study, sources of operational uncertainties will be limited to variations in operating temperatures and pressures only.

6.6. Sensitivities Due to Temperature Change

The operating temperatures of the fractionation columns are usually manipulated to meet product requirements, as well as to compensate for seasonal changes in the ambient temperature. Fluctuations in the cooling water supply temperature to the overhead exchanger have a direct effect on the overhead receiver temperature where sour water is in equilibrium with the process fluid. Actual experience in operating such processes indicates that the concentration of contaminants decreases at higher operating temperatures and vice versa. This is due to the thermodynamic characteristics / physical behaviour of some of the contaminants such as hydrogen sulphide and ammonia. Hydrogen sulphide and ammonia become more volatile with increase in temperature and tend to escape with the vapour split. This results in lower load of contaminants in the hydrocarbon liquid phase. Since water is also condensed along with the hydrocarbons, contaminants tend to accumulate in the water phase due to the higher solubility of contaminants in water in comparison to the hydrocarbon phase. From the above, it is clear that contaminant load in the waste water is a function of vapour liquid equilibrium and liquid – liquid equilibrium. Most of the time vapour – liquid equilibrium is controlling. Therefore at higher temperature hydrogen sulphide and ammonia tend to escape with the vapour split, leaving a lower load of contaminants to be washed by water. At the same time, the solubility of contaminants in water increases at higher temperature. Such a dual effect is thereby an interesting source of uncertainty.

Effects of variations in ambient temperature and operating pressure on the concentrations of the contaminants for each water-using unit have been monitored for one year. This involved analyzing water samples, which were collected daily, to determine the concentrations of various contaminants. For illustrative purposes, a typical crude unit is considered. Sample data for the overhead cooler of the crude distillation unit (CDU) which is cooled by seawater is shown in Figure 6.5. This plot demonstrates clearly that hydrogen sulphide concentration increases at low cooling seawater temperatures and vice versa.

Collected plant data was found to be insufficient for quantifying and modelling the effect of uncertainty in operating conditions on the concentrations of the contaminants. In order to be more representative and accurate , the prediction model should cover a wider range of variations and consider combinations of various sources of uncertainty. For this reason, a process simulator (SIMSCI, PRO II) was used to estimate the quantities of sour water produced and the concentration of contaminants for various operating conditions. Simulation results were compared with the actual concentration measurements (see

Figure 6.5) and found to be reasonably close. Finally, a number of correlations were obtained, from the simulation results, for estimating the load of the contaminants as a function of operating temperature and pressure.

As a result, each water-using unit has been associated with a set of correlations capable of predicting the concentration of the contaminants, for different intervals of operating conditions. Computational difficulties were avoided by formulating the correlations as linear functions of temperature and pressure. For certain instances, linearity was achieved by dividing the operating horizon into fine intervals and deriving the correlation for each interval. Detailed correlations for CDU are provided in Appendix C of the report. The correlations were then incorporated in the deterministic optimization model referred to as Case -3 in Chapter-5 and represented as GAMS expressions. Table 6.6 shows sample results of deviations in the loads of various contaminants for a temperature change of only 2°C below and 2°C above the nominal operating temperature, which is 37°C. The case studies (*Case-0* to *Case-3*) presented in Chapter 5 earlier, are for a 37°C operating temperature. It is clear that deviations are not the same for all units. This provides an excellent indication that the uncertainties considered in this study are not artificial, but are rather extracted from actual operation of process units. Note that the loads listed in Table 6.6 are for uncertainty in the temperature of the overhead of the fractionation column.

Table 6.6: Contaminant loads (kg/hr) at different operating temperatures.

Unit	**Low: 35°C**		**Normal: 37°C**		**High: 39°C**	
	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3
CDU	5.1	20.6	4.8	20.8	4.5	21.0
VDU	4.3	3.2	4.0	3.2	3.8	3.2
TGT	41.5	30.4	41.2	31.4	40.7	32.3
HCR	448.9	218.3	442.2	217.2	434.8	216.0
GOD	51.0	13.2	49.6	13.2	48.2	13.1
ARD	2902.8	1872.7	2870.4	1871.3	2837.3	1869.3
KD	1.8	0.9	1.7	0.9	1.7	0.9
FCC	54.6	5.5	54.6	5.5	54.6	5.5
DES	0.9	9.1	0.9	9.1	0.9	9.1

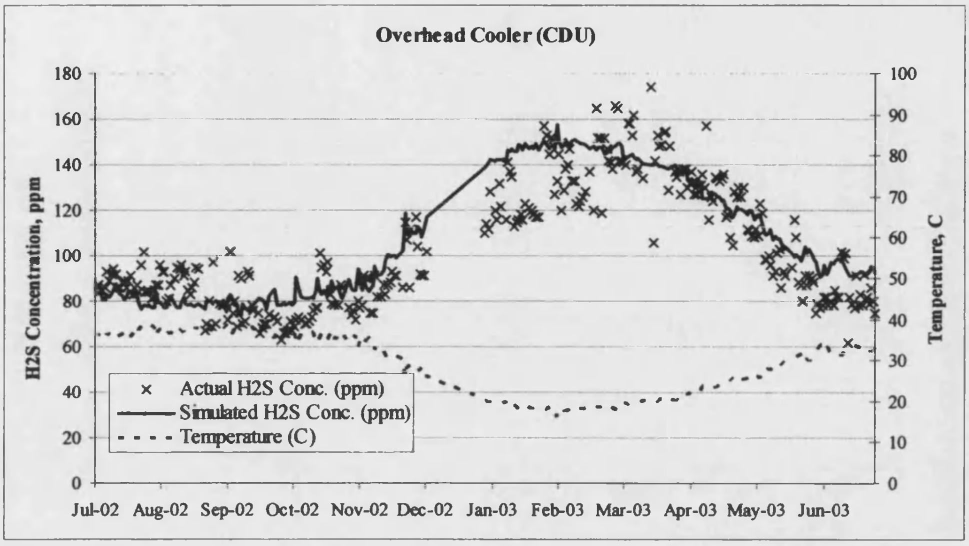


Figure 6.5: Variations of hydrogen sulphide content in the wastewater from the overhead of the CDU unit with seawater cooling temperature.

Column overhead operating temperature is changing from unit to unit. Each unit's overhead trim condenser utilises seawater as the cooling media, thereby any change in the seawater temperature will correspondingly change the respective process unit's condensing temperature. This change in condensing temperature changes the contaminant mass load. In order to simplify the calculation for prediction purposes in the model, it is proposed to use a temperature ratio instead of the actual temperature. Furthermore, the ratio of cooling water temperature is taken to be directly proportional to the ratio of operating temperature. Operating temperature information is proprietary in nature, and so is not disclosed. Therefore it was decided to use ratio of cooling water temperature as it is common for all units. A correlation for predicting the concentration of impurities is now based on the temperature ratio and it will be uniform across all units.

6.7. Sensitivities Due to Pressure Change

Table 6.7 shows sample results of deviations in the loads of various contaminants for a pressure change of 5% below and 5% above the nominal operating pressure. The case studies (*Case-0* to *Case-3*) presented in chapter 5 are for the nominal/design operating pressure. Operating and design pressures are not disclosed due to proprietary reasons. It is clear from Table 6.7, that deviations are not the same for all units. As for temperature, this provides an excellent indication that the uncertainties considered in this study are not artificial, but rather are extracted from actual industrial practice. Note that the loads listed in Table 6.7 are for uncertainty in the pressure of the overhead of the columns/ separators. The concentration of contaminants for the Desalter (DES) units is not affected by the pressure variations, since Liquid-Liquid-Equilibrium is not affected due to change in pressure and Desalter (DES) is handling only liquid.

Table 6.7: Contaminant loads (kg/hr) at different operating pressure.

Unit	Low: -5%		Normal:		High: +5%	
	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3
CDU	4.57	20.72	4.8	20.8	5.03	20.88
VDU	3.97	3.19	4.0	3.2	4.03	3.21
TGT	40.38	31.40	41.2	31.4	41.69	31.40
HCR	441.41	217.07	442.2	217.2	442.98	217.32
GOD	49.01	13.19	49.6	13.2	50.40	13.21
ARD	2799.21	1864.12	2870.4	1871.3	2939.41	1878.65
KD	1.70	0.90	1.7	0.9	1.70	0.90
FCC	54.60	5.50	54.6	5.5	54.60	5.50
DES	0.90	9.10	0.9	9.1	0.90	9.10

From the above it is clear that an increase in pressure increases the level of impurities in sour water whereas an increase in temperature has the opposite effect. Furthermore, the magnitude of the variation is different for each unit. This is mainly due to volatility and equilibrium concentration of ammonia and hydrogen sulphide being different at various pressures in the vapour-liquid equilibrium. Liquid-liquid equilibrium does not depend on pressure but is affected by change in temperature.

It is pertinent to note that most of the reuse water originates from VDU /CDU. Hence, any changes in impurities from these units will have major impact, since they will change the reuse water quantity. However a similar effect does not arise for water from ARD and HCR as this water is high in hydrogen sulphide and ammonia and cannot be reused without regeneration.

Therefore it is important to study the real sensitivity of operating changes for the actual of refinery case.

6.8. Sensitivity Analysis Results

Four sensitivity analysis cases have been conducted to study the effect of uncertainties in operational conditions on the optimal wastewater network. The first two cases (*Case-4* and *Case-5*) assume that the operating temperature of cooling media varies from 32°C in winter to 42°C in summer, respectively, keeping operating pressures fixed at nominal (design) values. The other two cases (*Case-6* and *Case-7*) assume ±5% deviations in operating pressure from the nominal (design) conditions, while the operating temperature is fixed at 37°C. Optimal wastewater networks for these cases have been determined using the deterministic model together with the developed correlations. The optimization results are summarized and compared later in Table 6.12 against the reference case, *Case-3*.

The optimization results of various wastewater networks are compared using two criteria. The first is the freshwater demand, whilst the second is the amount of wastewater reuse and regeneration-reuse. The latter provides an indication as to whether a modification of topology (i.e. changes to connections between different units) is required. Accordingly, a network design which is resilient to variations in operating conditions is the network that is capable of accommodating changes in freshwater demands, and with a flexible topology to account for variations in wastewater reuse and regeneration reuse.

The sensitivity analysis results shown in Tables 6.8 and 6.9 reveal that for a change in temperature (5°C decrease or 5°C increase in operating temperature from 37°C), two scenarios (*Case-4* to *Case-5*) demand the minimum freshwater amount, i.e, 143.6 tonnes/hr. Hence, freshwater is only used for steam generation. However, the results related to wastewater reuse from the fractionation units, CDU and VDU, indicate that topology modifications might be necessary. For a 5°C decrease or 5°C increase in operating temperature, the amounts of direct reuse from the CDU to different units decreased by 35% and increased by 11.8%, respectively, as CDU is the marginal supplier of additional reuse water. Conversely, reuse amounts from the VDU unit are not affected. Existing regenerator capacity is limited to 165 tonnes/hr. Any additional regeneration capacity required has to be built and integrated with the existing unit. The cost of additional regeneration capacity is expected to be much higher, around (2 KD / m^3) compared to cost of fresh water (0.6 KD / m^3). Additional regeneration cost is higher mainly due to the following:

1. The additional regeneration requirement is small compared with existing capacity.
2. Modifications need to be carried out in a highly congested area.

For Case -4, however it is economical to increase the regenerator capacity compared to fresh water. It was found that overall the cost increases to 1.328 MMKD/yr when the regenerator size is restricted to 165 tonnes/hr. This will be further elaborated in the next Chapter.

Table 6.8: Sensitivity case with operating temperature 32°C *Case-4*

	Steam	Fresh water	Waste water			Reuse from	
	T/hr	T/hr	To Regen.	To Treat.	From Regen.	CDU	VDU
Boiler	–	143.63	–	4.18	–	–	–
CDU	52.50	–	38.21	4.05	0.24	–	0.76
VDU	45.35	–		–	–	–	–
TGT	27.20	–	27.20	–	–	–	–
KD	1.80	–	4.50	–	0.08	0.42	2.20
GOD	6.50	–	14.90	–	0.25	0.97	7.18
HCR	1.00	–	17.20	–	0.69	9.87	5.64
ARD	0.50	–	68.90	–	38.83		29.57
FCC	4.50	–		18.10	13.60	–	–
DES	0.10	–		91.32	91.22	–	–
GEN1	–	–		25.98	25.98	–	–
Total	139.45	143.63	170.91	143.63	170.90	11.25	45.35

Table 6.9: Sensitivity case with operating temperature 42°C *Case-5*

	Steam	Freshwater	Wastewater			Reuse from		
	T/hr	T/hr	To Regen.	To Treat.	From Regen.	KD	CDU	VDU
Boiler	–	143.63	–	4.18	–	–	–	–
CDU	52.50	–	34.55			–	–	1.00
VDU	45.35	–		–	–	–	–	–
TGT	27.20	–	27.20	–	–	–	–	–
KD	1.80	–	2.26	–		–	0.41	2.29
GOD	6.50	–	14.90	–		0.78	0.78	6.84
HCR	1.00	–	17.19	–		1.46	9.82	4.93
ARD	0.50	–	68.90	–	30.15	–	7.94	30.30
FCC	4.50	–		18.10	13.60	–	–	–
DES	0.10	–		91.32	91.22	–	–	–
GEN1	–	–		30.03	30.03	–	–	–
Total	139.45	143.63	165.00	143.63	165.00	2.24	18.95	45.35

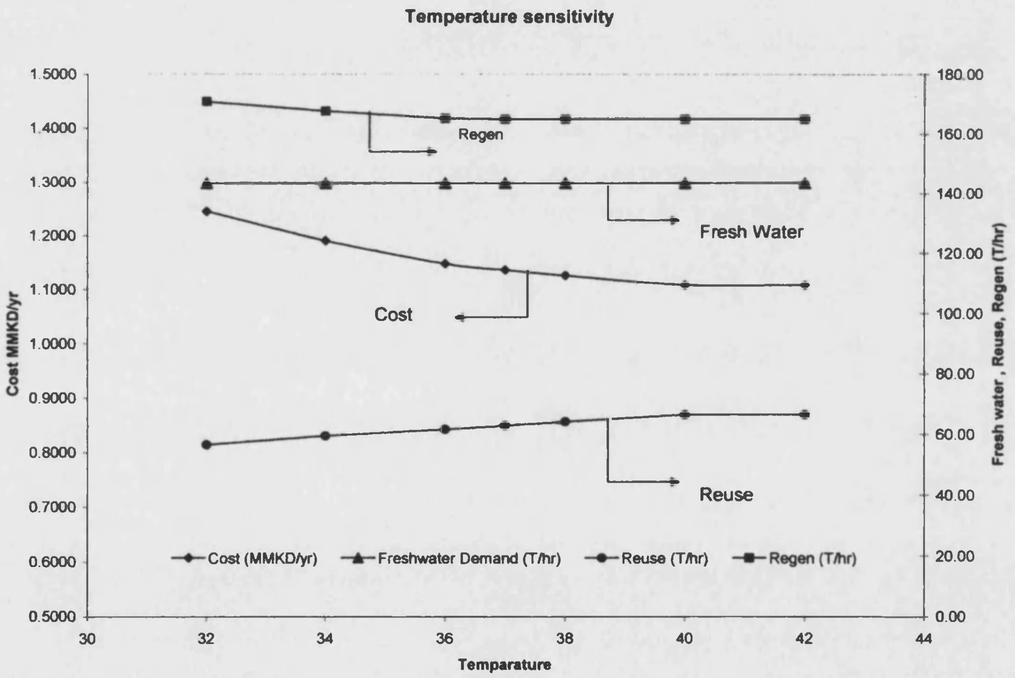


Figure 6.6: Changes in cost, freshwater demand and direct reuse for deviations in temperature °C (Cases-3,4,5)

The total fresh water requirement for Case -5 is similar to that for the base case (Case 3), since fresh water is used only for steam production. The regenerator is fully saturated and reuse is slightly higher as a result of reduced contaminant level in the outlet of each unit. Due to the above reasons the total cost for this case has reduced to 1.108 MMKD/yr as shown in Figure 6.6, even though there is 5°C increase in temperature and a corresponding decrease in contaminant concentration

The sensitivity analysis results for Case-6 and Case -7 for -5% decrease and +5% increase in base case pressure while operating temperature is fixed at 37°C is listed in Table 6.10 and 6.11 respectively.

Table 6.10: Sensitivity case with change of -5% in pressure *Case-6*

	Steam	Freshwater	Wastewater			Reuse from	
	T/hr	T/hr	To Regen.	To Treat.	From Regen.	CDU	VDU
Boiler	–	143.63	–	4.18	–	–	–
CDU	52.50	–	5.49		0.09	–	0.91
VDU	45.35	–	26.83	1.95	–	–	–
TGT	27.20	–	27.20	–	–	–	–
KD	1.80	–	4.50	–		0.31	2.39
GOD	6.50	–	14.90	–		0.95	7.45
HCR	1.00	–	17.20	–		10.37	5.82
ARD	0.50	–	68.89	–	32.02	36.39	
FCC	4.50	–		18.10	13.60	–	–
DES	0.10	–		91.32	91.22	–	–
GEN1	–	–		28.07	28.07	–	–
Total	139.45	143.63	165.00	143.62	165.00	48.01	16.57

Decrease in pressure (Table 6.10) reduces the contaminants in the outlet of CDU / VDU, which increases the reuse quantity slightly. The regenerator is also fully utilized in these cases. Reuse from both the units varies widely with variations in operating pressure. Reuse from CDU increased to 48.01 tonnes/hr and reuse from VDU reduced to 16.57 tonnes/hr. This is mainly due to changes in relative volatility of contaminants in the vacuum unit and the crude unit for the change in operating pressure. From Table 6.10 and

6.11, it can be inferred that an increase in pressure at the CDU has a higher impact on contaminant concentrations compared to the VDU, for the same variation in pressure. However overall reuse is slightly increased and cost remains marginal at 1.123 MMKD/yr as shown in Figure 6.7. Thus, reduction in pressure does not have a major impact, either on cost or on fresh water flow.

Table 6.11: Sensitivity case with change of +5% in pressure *Case-7*

	Steam	Freshwater	Wastewater			Reuse from		
	T/hr	***T/hr***	***To Regen.***	***To Treat.***	***From Regen.***	**KD**	**CDU**	**VDU**
Boiler	–	143.63	–	4.18	–		–	–
CDU	52.50	–	33.10	4.21	0.12		–	0.88
VDU	45.35	–		–	–		–	–
TGT	27.20	–	27.20	–	–		–	–
KD	1.80	–	3.71	–			0.43	2.28
GOD	6.50	–	14.90	–		0.28	1.13	6.99
HCR	1.00	–	17.20	–		0.43	10.77	5.01
ARD	0.50	–	68.90	–	34.32		3.87	30.21
FCC	4.50	–		18.10	13.60		–	–
DES	0.10	–		91.32	91.22		–	–
GEN1	–	–		25.73	25.73		–	–
Total	139.45	143.63	165.00	143.55	165.00	0.71	16.19	45.35

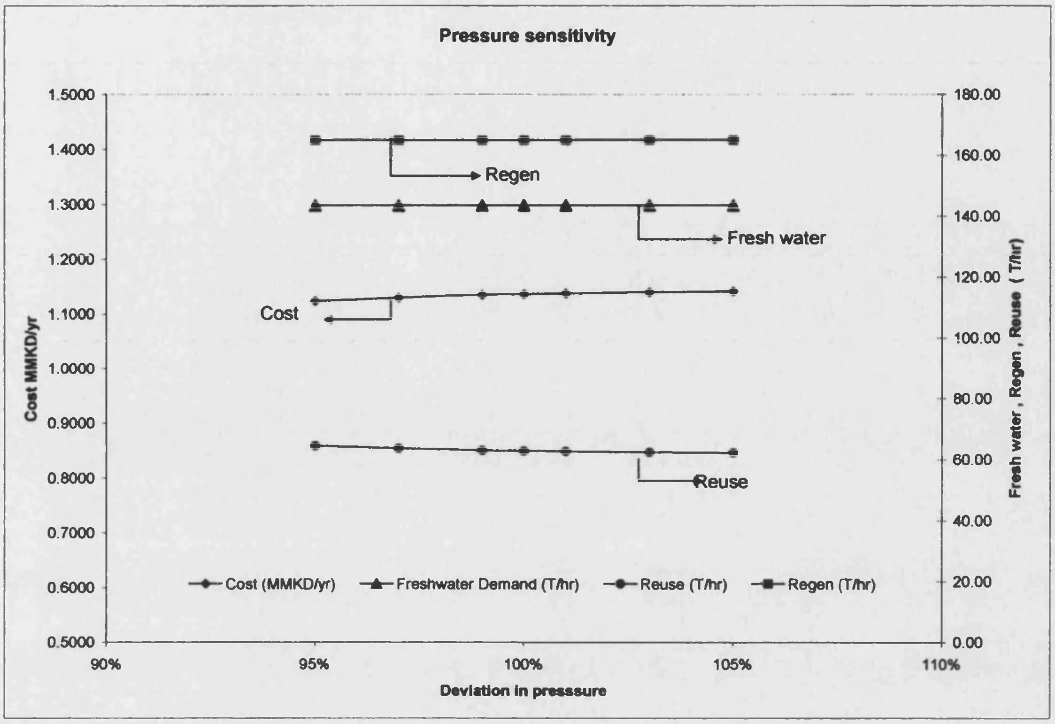


Figure 6.7: Changes in cost, freshwater demand and direct reuse for deviations in Pressure

An increase in pressure by 5% (Table 6.11) did not change the topology and fresh water flow, i.e., reuse flows are similar to the base case. Therefore, an increase in pressure by 5% increases the cost only by about one percentage. Compared with Case -6, reuse flow rate were flipped between VDU and CDU because of change in relative volatility. For a better illustration, all the above four sensitivity cases (case-4,5,6,7) are summarised below.

Table 6.12: Sensitivity analysis results

Case	Condition	Freshwater	Reuse from[1]		Cost
		tonnes/hr	*CDU*	*VDU*	*MMKD[2]/yr*
Case-3	Ref. 37°C	143.6	16.62	45.46	1.136
Case-4	32°C	143.6	11.25	45.35	1.245
Case-5	42°C	143.6	18.95	45.35	1.108
Case-6	-5% Press.	143.6	48.01	17.57	1.123
Case-7	+5% Press.	143.6	16.19	45.35	1.141

[1]Reuse from KD to GOD and HCR is also needed for Case-5 and Case-7

[2]1 KD (Kuwaiti Dinar) = US$ 3.3

It is clear from the sensitivity analysis results that the topology of the optimal wastewater network would vary significantly as a result of uncertainty in operating temperature and pressure. The results of the reference case, *Case-3*, show that wastewater from the CDU and VDU units are reused in various units. If the wastewater network is designed based on these results, then slight deviations in operating conditions would result in a network incapable of handling the demanded flow rates.

6.9. Conclusion

Due to ever changing market requirements, product demand and specifications keep changing. To meet these requirements operating conditions are varied to meet the primary goal of profitability. Therefore plant and its sub systems such as the water network has to be resilient and robust for changes in the operating requirements.

To start with , sensitivity analysis was carried out for three literature examples with reuse only. All these examples show proportional changes in fresh water demand and cost. It can be concluded that even a stochastic optimization approach would result in the same network structures and linear dependence on freshwater demands. However, this conclusion cannot be generalized due to critical assumptions made such as reuse only, no constraints in waste water quality, and equal changes in mass load for all contaminants.

As a second step, a fourth literature example with a regenerator was considered. In this example, contrary to the other three examples, reuse water, regeneration water and freshwater change disproportionately with change in mass load. This reveals a non linear behaviour of the network and hence existence of scope for optimisation under uncertain operating conditions.

All the above cases are only hypothetical in nature because the mass load is fixed. In real life situations, operational temperature and pressure govern the outlet concentrations of contaminants.

Finally , to access the behaviour of the deterministic model (Case -3) in realistic situations , sensitivity analysis was carried out for changes in temperature of ±5°C and in pressure of ±5%. Cost for lower temperature operation is 109% of base cost and for higher temperature is about 97.5%. Similarly for change in pressure of -5 % and +5%, the cost is 98.8 % and 100.4 % respectively of the base case.

It is clear from the sensitivity analysis results that the topology of optimal wastewater networks would vary significantly as a result of uncertainty in operating temperature and pressure. The results of the reference case, *Case-3*, given in Table 5.5, show that wastewater from the CDU and VDU units are reused in various units. If the wastewater network is designed based on these results, then slight deviations in operating conditions would result in a network incapable of handling the demanded flow rates. The uncertainties of the real life situation for this model are further developed into the stochastic formulation which is described in Chapter 7.

Chapter Seven

7. STOCHASTIC MODEL

7.1. Introduction

In the previous chapter, sensitivity analysis was carried out for various examples and it was concluded that for simpler mass load models, the fresh water demand and total cost are linearly related to mass load changes. In contrast, addition of a regenerator made fresh water demand and cost change non-linearly with mass load changes. As these cases are hypothetical, the sensitivity analysis was carried out on the deterministic model (Case -3) and it was found that it is sensitive to changes in temperature and pressure. Normally designers use the worst case for designing the network system (eg. Case-4, with a 5°C decrease in temperature). However, the solution optimised for this case may not be the optimum for the whole period. Considering the fact that unit operating conditions change due to many uncertainties, units and the available hardware have to be robust to meet the requirements and the best solution must be obtained for the entire period. If the uncertainties or changes are known in advance, then the best solution can be obtained. However in the real life situation, the future is always uncertain with continuous and sometimes unpredictable changes. Stochastic formulation identifies the minimum cost that can be achieved if the future is unknown.

If one has perfect information about stochastic components of the problem, then the Excepted Value of Perfect Information (EVPI) can be calculated. This indicates how much more one can expect to gain if future changes are known definitely. In other words, EVPI measures the value of knowing the future with certainty. Therefore, EVPI is the maximum that can be spent in gathering information about the uncertain world.

Stochastic Design involves designing the network, while Stochastic Operation involves decisions on the inventories (flow rates) for fixed freshwater resources after modifying the network based on stochastic design. For the former, direct wastewater reuse may be considered as the first-stage decision variable, whilst freshwater demands and regeneration-reuse amounts are the second-stage variables. Stochastic operational solutions are needed for cases when resources are limited, as well as for planning purposes.

7.2. Stochastic Optimization

It is evident from the sensitivity analysis results presented in chapter 6, that the optimal wastewater network is significantly affected by even slight variations in operating temperature and pressure. Due to the fact that nominal conditions are varied widely to meet yield and throughput requirements, and perfect operational information is not always available, it is useful to determine a wastewater network that is both economical and at the same time flexible to operate. We will demonstrate here how stochastic programming may be used to determine such a network.

In practice, two type of problem may be identified. The first one involves designing the network, while the second problem involves decisions on the inventories (flow rates) for fixed freshwater resources. These problems will be termed "Stochastic Design" and "Stochastic Operational" problems.

For the former, direct wastewater reuse is considered as the first-stage decision variable, whilst freshwater demands and regeneration-reuse amounts are the second-stage variables. Stochastic operational solutions are needed for cases when resources are limited, as well as for planning purposes. For these instances, it would be useful to determine the optimal freshwater demands that will minimize the cost of the wastewater network in the presence of uncertainties. In this case, freshwater demands, reuse and regeneration-reuse amounts are considered as decision variables.

Stochastic design problems are more effective in developing resilient wastewater networks, and at the same time applicable for both grassroots design and retrofit problems. Nonetheless, operational stochastic problems may be applied to existing wastewater networks to study variations in freshwater demands and capacities of regeneration and treatment plants.

The approach used for both stochastic design and stochastic operational problems is two-stage stochastic non-linear programming with fixed recourse. The stochastic programming model is solved for ±5°C deviations in the operating temperature.

Accordingly, for a period of one year, three scenarios are considered: low, average and high corresponding to 32°C, 37°C and 42°C, respectively. It is also assumed that the probabilities of occurrence of these three scenarios are 25%, 50% and 25%, respectively. This means that low and high temperatures are expected for three months each, whilst normal operating conditions are expected for six months.

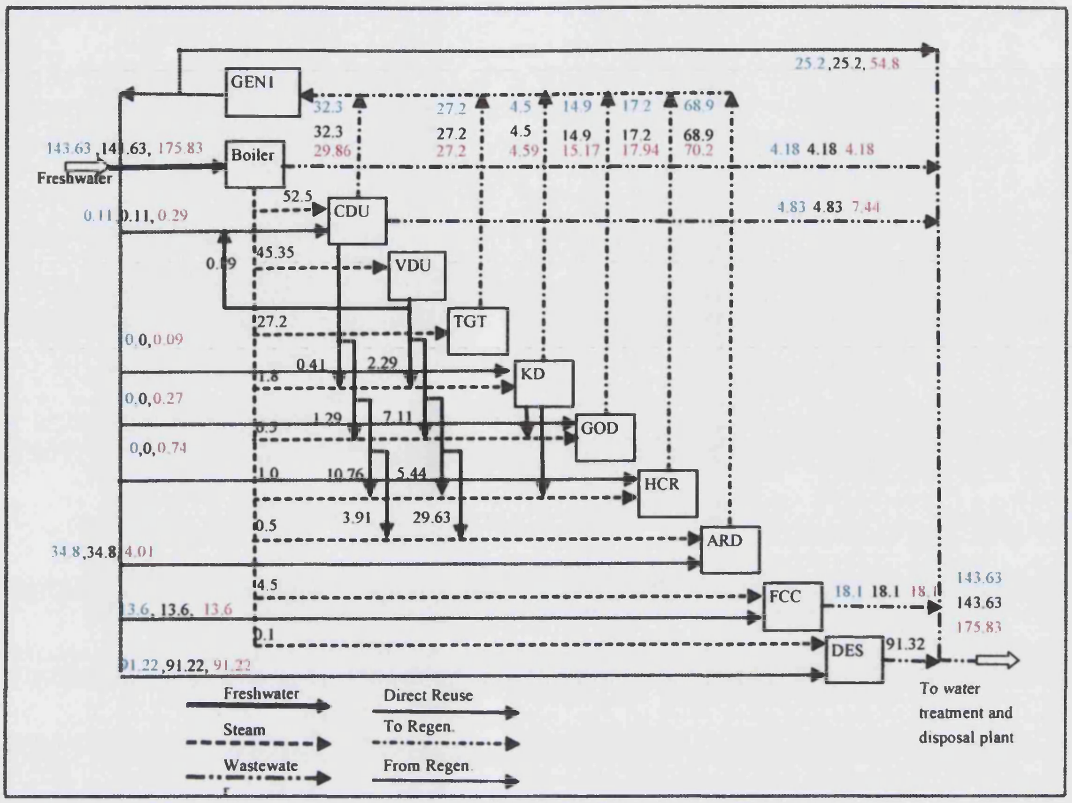
7.3. Stochastic Design Problem

For this problem, it is required to determine the optimal network design (topology or connectivity) that will minimize the effect of uncertainty in operating temperature on the minimum cost of the network. Accordingly, the first-stage decision variables are the amounts of direct reuse between the process units, and so the freshwater demands will be considered as second-stage decision variables.

Table 7.1: Stochastic Optimization Design results, Case-8

Units	Steam *T/hr*	Freshwater *T/hr*			Wastewater *To Regen.*		
		high	*average*	*low*	*high*	*average*	*low*
Boiler	–	143.63	143.63	143.63			–
CDU	52.50				32.30	32.30	29.86
VDU	45.35						
TGT	27.20				27.20	27.20	27.20
KD	1.80				4.50	4.50	4.59
GOD	6.50				14.90	14.90	15.17
HCR	1.00				17.20	17.20	17.94
ARD	0.50			32.20	68.90	68.90	70.25
FCC	4.50						
DES	0.10						
GEN1	–	–	–	–			
Total	139.45	143.63	143.63	175.83	165.00	165.00	165.00

Units	Reuse from CDU	Reuse from VDU	*To Treat.*			From Regen.		
			high	*average*	*low*	*high*	*average*	*low*
Boiler	–	–	4.18	4.18	4.18			–
CDU	–	0.89	4.83	4.83	7.44	0.11	0.11	0.29
VDU	–	–						
TGT	–	–						
KD	0.41	2.29						0.09
GOD	1.29	7.11						0.27
HCR	10.76	5.44						0.74
ARD	3.91	29.63				34.87	34.87	4.01
FCC	–	–	18.10	18.10	18.10	13.60	13.60	13.60
DES	–	–	91.33	91.33	91.33	91.23	91.23	91.23
GEN1	–	–	25.20	25.20	54.78	25.20	25.20	54.78
Total	16.37	45.35	143.63	143.63	175.83	165.00	165.00	165.00



Legend. High (Left /Top) Average (centre/ middle) : Low (Right / bottom) :

Figure 7.1: Stochastic design results flow sheet of water using units

The stochastic optimization results for this case (case-8) are presented in Table 7.1. and the flow sheet of water using units is illustrated in Figure 7.1. In this case, the amounts of wastewater reused are considered as first-stage variables. This resulted in determination of optimum topology (connectivity) between units that would accommodate the consequences of variations in operating temperature. Additionally, the stochastic program determined the maximum freshwater demand (175.8 tonnes/h), which will be necessary in case the worst scenario is expected to occur. This means that 32.2 tonnes/h of fresh water should be readily available for use as per the requirement in addition to the condensing steam (143.6 tonnes/h).

The optimal solution can be understood as follows: at the nominal operating condition, condensing steam would be sufficient enough to satisfactorily remove the contaminants. Variations in the operating conditions will however result in disturbance to the reuse and regeneration-reuse amounts, which need to be compensated by the additional freshwater utilization not exceeding 32.2 tonnes/h. Additional fresh water is consumed only in ARD , since it is the major consumer of water other than the desalter. Reduction in inlet concentration to ARD will increase the reuse. However the same is not true with the desalter. This clearly demonstrates that the model is robust and utilizes all the available opportunities to find the lowest cost solution.

This solution demonstrates that it is impossible, under conditions of uncertainty, to find a solution that is ideal under all circumstances. Condensing steam needs to be supplemented by a surplus freshwater amount that may or may not be needed. Such decisions can appear in a stochastic model because decisions have to be balanced or hedged against various uncertain scenarios.

The hedging effect has an important impact on the expected optimal cost. The optimal cost of the stochastic case, Case-8, is 1.198 MM KD/yr, which lies between the costs of *Case-4* and *Case-5*. Assuming that perfect information is available about variations in operating conditions, one would provide a different operational procedure for each scenario. The annual cost of the combined scenarios would then be evaluated as the weighted average of three costs, namely 1.156 MM KD/yr. This is based on the weighted average cost of Case 3 , Case 4 and Case 5. (The possibilities of occurrence of temperatures are 25% for 32°C, 50% for 37°C and 25% for 42°C). This is the cost realized under perfect information.

Since we have no prior information on the occurrence of uncertainties, the best option is to design the network based on the stochastic solution, Case-8. This results in a network with optimal cost of KD 1.198 MM KD/yr. The difference between this cost and the perfect information cost, namely KD 42,315 KD/yr is called the *expected value of perfect information* (EVPI). This additional cost is due to the presence of uncertainty. The EVPI with this particular refinery example is only 3.5% of the optimal cost of the network, and is exceptionally low. It means that by knowing the future with absolute certainty , we can only reduce the cost by 3.5%

As per sensitivity analysis, the fresh water demand has not increased for case-4 and has remained at 143.6 tonnes/hr. Nonetheless, the regenerator size has increased to 170.91 tonnes/hr in spite of the high regeneration cost (2 KD / m^3). This is due to the additional capacity requirement. However, in the stochastic analysis, the model predicted that it is preferable to increase the fresh water requirement during that period when the temperature is low, instead of installing additional regeneration facilities which will not be utilized for average and high temperature seasons. In order to check the model, another sensitivity case was run by limiting the regenerator size to 165 tonnes/hr. The fresh water requirement for this case increased to 171.2 tonnes/hr resulting in a total cost of 1.328 MMKD/yr compared to the Case-4 cost of 1.248 MMKD/yr.

This clearly indicates that an additional regenerator is not the best option as per the stochastic model. Thus stochastic model is helpful in predicting the investment options too.

7.4. Stochastic Operational Problem

After the topography and geographical frame work are finalised, the fresh water demand can be optimised based on scenario changes.

Based on the results of stochastic design, reuse from one unit to another is finalised, hardware for this is installed and an additional regenerator is not considered. Reuse was fixed up to the maximum amount as per the stochastic design problem results. Regenerator capacity is limited to the existing capacity. Fresh water demand is allowed to vary for different scenarios. The minimum cost was calculated using the model and the results are tabulated in Table 7.2.

Fresh water is higher for the low temperature or high concentrations case, since reuse is allowed to change for each case unlike in the stochastic design problem where reuse is kept the same for all scenarios. For the stochastic operational problem the fresh water requirement is slightly lower than the stochastic design for the worst case scenario alone. The cost for this case is 1.194 MMKD/yr.

Table 7.2: Stochastic Optimization (Operational) , Case-9

Units	Steam	Freshwater			Wastewater					
	T/hr	*T/hr*			*To Regen.*			*To Treat.*		
		high	*average*	*low*	*high*	*average*	*low*	*high*	*average*	*low*
Boiler	–	143.63	143.63	143.63			–	4.18	4.18	4.18
CDU	52.5			0.22	32.30	32.30	32.30	4.82	4.83	6.65
VDU	45.35									
TGT	27.2				27.20	27.20	27.20			
KD	1.8			0.07	4.50	4.50	4.50			
GOD	6.5			0.23	14.90	14.90	14.90			
HCR	1			0.63	17.20	17.20	17.20			
ARD	0.5			29.15	68.90	68.90	68.90			
FCC	4.5							18.1	18.1	18.1
DES	0.1							86.76	91.33	95.89
GEN1	–	–	–	–				29.76	25.2	49
Total	139.45	143.63	143.63	173.94	165.00	165.00	165.00	143.63	143.63	173.82
Units					**Reuse from**					
		From Regen.			**CDU**			**VDU**		
		high	*average*	*low*	*high*	*average*	*low*	*high*	*average*	*low*
Boiler				–				–		–
CDU		0.11	0.11					0.89	0.89	0.78
VDU										
TGT								–		–
KD					0.41	0.41	0.34	2.29	2.29	2.29
GOD					1.29	1.29	1.06	7.11	7.11	7.11
HCR					10.76	10.76	10.13	5.44	5.44	5.44
ARD		34.87	34.87	6.61	3.91	3.91	3.02	29.63	29.63	29.63
FCC		13.60	13.60	13.60				–		–
DES		86.66	91.23	95.79				–		–
GEN1		29.76	25.20	49.00				–		–
Total		165.00	165.00	165.00	16.37	16.37	14.55	45.35	45.35	45.24

The stochastic operational case is similar to the stochastic design as topology is restricted to the same as that of the design case. For the same topology an improvement is possible, and so there is a reduction in cost of 4,400 KD/yr for the operational case in comparison with the stochastic design case. The expected reduction in cost is the additional profit which can be achieved by adjusting the operating parameters after fixing the topology. This is small basically because the inbuilt design margin takes care of high and average scenarios. For other refinery cases , where the regenerator is constrained, the profits could be much higher.

7.5. Conclusion

Sensitivity analysis carried out in the previous chapter and results for various cases indicate that wastewater minimization under uncertainties requires optimal design of wastewater networks which should be resilient to variations in operational conditions.

Considering the continuous and unpredictable changes in real life situations, a stochastic formulation has been developed based on scenario-analysis. A stochastic programming approach (stochastic design and stochastic operational problems) has been considered with different first and second stage variables to arrive at either the optimal network design (topology or connectivity) or minimum fresh water demands for an existing design. The probability of occurrence of various scenarios is incorporated and fitted to the model.

Thus stochastic analysis helps in identifying the minimum cost solutions for the design stage as well as for planning the existing network operation as demonstrated in Sections 7.3 and 7.4. In addition, stochastic analysis can be applied and utilized effectively in deciding the investment options also as indicated in Section 7.3 (Network with regenerator example).

Stochastic design model produced a network with an optimal cost of 1.198 MM KD/yr. The cost for this solution is higher than the perfect information cost by 42,315 KD/yr (EVPI). The EVPI with this particular refinery example is only 3.5% of the optimal cost of the network. This is exceptionally low.

As per the model, the regeneration capacity increased to 170.91 tonnes/hr for the worst case and the fresh water use increased to 173.9 tonnes/hr for the stochastic case based on optimisation cost. This gives an interesting insight on how this model can be used even for investment decisions.

The stochastic operational model is used to optimise the network after modifications are carried out based on stochastic design. Therefore, in order to further optimise the fresh water resources, the stochastic operational problem was solved for the same topology as the design case. It is evident from the results that overall the cost can be further reduced by adjusting the reuse and fresh water flow to the extent of 4,400 KD/yr.

From the results of the stochastic design and operational models dealt with in this chapter, it can be safely concluded that by running the stochastic program, it is possible to arrive at the decision which is expected to cost much less than the worst case scenario. This can also be used effectively for making investment decisions like augmenting the capacity under all circumstances instead of the worst case scenario.

Chapter Eight

8. CONCLUSIONS AND FUTURE WORK

8.1. Overview

Industrial growth has resulted in a huge consumption of natural resources and the generation of considerable amounts of wastes including wastewater causing global environmental concerns. Accordingly, it is essential to reduce all types of waste not only to meet environmental regulations but also to stay competitive in industry. Since water is a scarce resource in the GCC countries, including Kuwait, and wastewater is a major pollutant from refinery operations, this thesis has focused on methods for minimizing wastewater generated from refineries and thereby reducing the freshwater requirement. The novelty of this research work is that it considers wastewater minimization under uncertain operating conditions using mathematical programming.

A mathematical optimization model for wastewater minimization has been developed. The model handles multiple contaminants and accommodates three pollution prevention options: direct reuse, regeneration-recycle, and regeneration-reuse. Two versions of the mathematical model have been used, namely, a deterministic model and a stochastic model. The deterministic model has been used to generate the wastewater networks for cases in which the operating conditions are fixed. On the other hand, the stochastic model has been used for decision making under uncertainty. Generally, the nature of all wastewater minimization models is nonlinear programming (NLP). The nonlinearity mainly arises from multiplying the water flow rate with the concentration of the contaminants. GAMS has been used in solving the optimization models.

The mathematical models were first validated against generic examples from the literature. The resulting wastewater networks were found to be broadly consistent with those reported in the literature. The capabilities of the proposed model were further demonstrated by introducing additional considerations such as the impact of the physical distances between different operations on the direct reuse option.

A typical refinery wastewater network has been considered as the main case study. The selected refinery network differs from the hypothetical examples found in literature in that it reflects actual operational practices in terms of the contaminants involved and their loads. Furthermore, steam-using units have been considered in addition to the direct water-using units. Condensing stripping steam is a major source of wastewater in refineries, and should not be ignored. The considered wastewater network consisted of nine major steam and water-using units in actual refinery operations.

8.2. Discussion and principal conclusions

Wastewater minimization in refinery operations has been investigated through four case studies. The base case (Case-0, against which other cases are compared) demands 342.1 tonnes/hr of freshwater. Three wastewater minimization options have been considered. In the first option (Case-1), the total freshwater requirement can be reduced by 22.7%, if part of the sour water generated from various process units is directly reused in other process units. The second option (Case-2) considers treating the sour water in a regenerator and recycling it back to the process units. This regeneration-recycle option resulted in reducing the freshwater demand by 47.7% compared with the base case. Complete integration has been achieved in the third option (Case-3). For this option, direct reuse has been combined with regeneration-reuse options. Consequently, savings in freshwater requirement amount to about 58%. In fact, wastewater generated from steam-using units has been found to be enough to satisfy the requirements of all water using units. In other words, the resulting optimum wastewater network for Case-3 demands freshwater for steam generation only. Further reduction in the amount of wastewater production is not possible because it is not feasible to reuse generated wastewater as boiler feed water. The examples and case studies have demonstrated the effectiveness of the proposed mathematical model in solving wastewater minimization problems.

Due to ever-changing market requirements, product demands and specifications keep changing. In actual refinery operations, this requirement is met by changing the operating conditions. Other sources for operational changes, and hence operational uncertainties, include seasonal weather variations, quality of crude feedstock and changes in product yields (due for instance to catalyst reactivity). In such an uncertain environment, optimum wastewater networks should be resilient and robust to changes in the operating conditions.

To illustrate the impact of uncertainty on the optimum wastewater networks, sensitivity analysis was carried out first for the literature examples. The amounts of fixed contaminant loads were varied below and above the nominal amounts. As a result, all examples showed proportional changes in fresh water demand and cost. Hence, it might be concluded that the proposed wastewater networks are resilient to changes in the concentrations of the contaminants. However, it was shown that this conclusion cannot be generalized due to the fact that these examples are hypothetical and not subjected to actual operational constraints found in practice. In addition, no constraints were considered on the wastewater quality, and only the direct reuse option was considered. Another critical assumption was that the mass loads of all contaminants were changed equally. This conclusion about resilience has been justified by considering another example from the literature, in which a regenerator has been included. In this example, contrary to the other three examples, the freshwater demands and wastewater flows of the network varied widely because of the equal changes in mass loads of the contaminants.

All the literature examples are considered to be hypothetical in nature mainly due to the fact that they assume fixed mass loads of contaminants. Unfortunately, this assumption is not applicable in actual refinery operations, where the inlet and outlet concentrations of contaminants are governed by operational conditions, such as operating temperature and pressure. A major contribution of the current work is that uncertainty in wastewater networks has been considered in the operating conditions rather than simply using fixed changes in the mass loads of the contaminants. This methodology may result in the creation of resilient wastewater networks, which can be practically applied in real refinery operations.

Operational uncertainties were first introduced as ±5°C changes in operating temperature and ±5% changes in operating pressure. This involved carrying out a sensitivity analysis study on Case-3. Values of the objective function increased by 9% and decreased by 2.5% (compared with the cost of Case-3) for –5 °C and +5° C changes in operating temperature, respectively. Similarly, for –5% and +5% changes in operating pressure, the cost of the optimum network varied slightly from –1.2% to 0.4%, respectively. These sensitivity analysis results showed clearly that the topology of the optimal wastewater network would vary significantly because of uncertainty in operating temperature and pressure. For instance, results of the deterministic case, Case-3, showed that wastewaters from the fractionators (CDU and VDU units) could be reused in various units. However, the sensitivity analysis results also showed that slight deviations in operating conditions would result in a wastewater network that is incapable of handling the demanded flow rates.

To account for continuous and unpredictable operational uncertainties in real life situations, the stochastic formulation has been developed. Two stochastic programming approaches have been attempted by considering different first and second stage variables. This resulted in both a design scenario and a planning scenario. The former produces an optimal network structure (topology), while the latter aims at determining the minimum freshwater demands for a given network. The probability of occurrence of various scenarios has been incorporated and has shown that the stochastic programming approach can help to identify the minimum cost solutions for both the design and planning cases. Furthermore, stochastic analysis would help in deciding on the investment options.

The stochastic design model produced a network with an optimal cost of 1.198 MM KD/yr (1 KD = US$ 3.3). The resulting expected value of perfect information (EVPI) for this particular refinery example is only 3.5% of the optimal cost of the network, which is exceptionally low with respect to the considered uncertainty. The optimum stochastic wastewater network revealed that freshwater demand has increased by 32.2 tonnes/hr for the worst case, whilst regeneration capacity has increased by 5.9 tonnes/hr for the corresponding worst case under sensitivity. The results provide an interesting insight into how this model can be used even for investment decisions.

The stochastic planning model has been applied to the stochastic wastewater network designed above in order to propose optimal freshwater resources. The results showed clearly that the overall cost of the network could be further reduced by adjusting the reuse and freshwater demands. This reduction in cost amounted to 4,400 KD/yr.

The overall conclusion is that uncertainty may have a significant effect on the optimal network design, and stochastic programming is an efficient approach for generating resilient networks, which are capable of handling uncertainties in operational conditions. The resulting wastewater networks have optimal design (topology) and at the same time demand the minimum freshwater amounts. In addition, the developed stochastic networks have exceptionally low EVPI, which may indicate low payback of the integration costs.

8.3. Future Work

As indicated earlier, refineries consist of complex integrated process units. Due to economic and marketing reasons, units are operated under different modes such as production of high sulphur (> 1% by wt) or low sulphur (< 0.5% by wt) fuel oil, or production of aviation turbine fuel or gas oil from the hydro cracker unit. Apart from different operating modes, some units are shut down or operated at varying capacity to increase the overall profitability of the refinery, due to economical and logistical reasons. Some refineries also process different types of crude oil based on their availability and market pricing. All the above operational changes contribute to change in quantity and quality of sour water produced. This further increases the type and quantum of uncertainty.

Based on the above discussion, future work should include quantifying and incorporating other sources of uncertainties in the design of the optimal wastewater network. Operating temperature and pressure have been considered as the main sources of uncertainty in this study. Other uncertainty sources may be investigated using the same methodology. Sources which should be considered include crude properties, refinery operating modes, and shutdown and start-up activities. Data collection is currently in progress as a first step for pursuing these proposed investigations.

Another important idea for future work is considering heat integration in designing the optimal wastewater network. Wastewater streams leave process units at different temperatures. At the same time, water-using units require specific inlet temperatures. It is believed that additional benefits may be claimed if the available energy is recovered rather than cooling or heating individual streams. Heat integration may be considered by modifying the optimization program. This involves adding an energy benefit item to the cost function, and including the energy balance equations as constraints in addition to maximum and minimum temperature limits on the inlet and outlet streams.

Wastewater minimization is an extremely important pollution prevention option in refinery operation. However, other pollution prevention options should be equally studied and investigated.

Nomenclature

$C^{in}_{m,i}$, $C^{out}_{m,i}$	Concentration of contaminant *m* in the inlet and outlet streams of unit/regenerator *i*, respectively, ppm
$C^{in,\max}_{m,i}$, $C^{out,\max}_{m,i}$	Maximum allowable concentration of contaminant m at the inlet and outlet of unit/regenerator i, respectively, ppm
$C^{out,\min}_{m,r}$	Minimum concentration of contaminant m in the outlet stream of regeneration unit r, ppm
C_{FW}	Unit cost of freshwater, KD/tonne
C_{RU}	Unit cost of direct wastewater reuse, KD/tonne
C_{RW}	Unit cost of wastewater regeneration-reuse, KD/tonne
C_{WT}	Unit cost of wastewater treatment and disposal, KD/tonne
$F_{i,j}$	Flow rate of direct wastewater reuse from unit *i* to unit *j*, tonnes/hr
$FG_{j,r}$	Flow rate of wastewater from regeneration unit *j* to another regeneration unit *r*, tonnes/hr
$FR_{i,r}$, $FR_{r,i}$	Flow rate of wastewater from water-using unit *i* to regeneration unit *r*, or from regeneration unit *r* to water-using unit *i*, respectively, tonnes/hr
FTR_r	Flow rate of wastewater from regenerator *r* to wastewater treatment and disposal plant, tonnes/hr
FTU_i	Flow rate of wastewater from unit *i* to wastewater treatment and disposal plant, tonnes/hr
FW_i	Flow rate of freshwater to water using unit *i*, tonnes/hr
KD	Kuwaiti Dinar, 1 KD = US$ 3.3
M	Set of contaminants
N	Set of water using units
R	Set of regeneration units
s	Scenario index
S_i	Flow rate of steam used in unit i, tonnes/hr

Greek Letters:

$\Delta w_{m,i}$	Mass load of contaminant *m* transferred from unit *i* to water stream, kg/hr
ω	Outcomes of random experiments
Ω	Set of all outcomes of random experiments

References

Al-Muzaini, S., Waste Minimization Program in Shuaiba Industrial Area, Wat. Sci. Tech., Vol. 39, No. 10-11, pp. 289-295, 1999.

Alva-Argaez.A, Vallianatos.A, Kokossis.A, A multi component transhipment model for mass exchange networks and wastewater minimization problems, Computers and Chemical Engineering Vol.23,1999.

Aguilera, N. and Nasini.G, Flexibility test for heat exchanger networks with uncertain flowrates, Comp. Chem. Engng., 19(9), pp. 1007-1017,1995.

Banares-Alcantara, R and Lababidi, H.M.S, "Design Support System for Process Engineering II KBDS : An Experimental Prototype", Computers Chem. Engg., Volume 19, No. 3,1995.

Bagajewicz, J. Miguel. A review of recent design procedures for water networks in refineries and process plants, Computer and Chemical Engineering Vol 24, pp. 2093 – 2113, 2000.

Bagajewicz J. Miguel and Savelski J. Mariano , On the necessary conditions of optimality of water utilizations systems in process plants with multiple contaminants, Chemical Engineering Science Vol. 58, pp. 5349 – 5362, 2002.

Bagajewicz J. Miguel, Rodera Hernán and Savelski Mariano, Energy efficient water utilization systems in process plants, Computers & Chemical Engineering, Vol. 26, Issue 1, pp. 59 – 79,15 January 2002.

Bagajewicz J. Miguel, Rivas Margioro , Savelski Mariano J. , A robust method to obtain optimal and sub-optimal design and retrofit solutions of water utilization systems with multiple contaminants in process plants, Computers & Chemical Engineering, Vol. 24, pp. 1461 – 1466, 2000.

Benforado, D.M., and Ridlehoover.G, Pollution Prevention-Firm's Experience, Chemical Engineering, Vol. 98, 1991.

Birge, J.R., and Louveaux.F, Introduction to Stochastic Programming, Springer Series in Operations Research, Springer-Verlag, New York, 1997.

Boden A., Water Conservation – an industry view, Water Supply, Vol 15, No. 4, pp. 17-20, 1997.

Bonom L., Nurizzo.C and Rolle.E, Advanced Wastewater Treatment and Reuse: Related Problems and Perspectives in Italy, Water Science Technology, Vol. 40, No.4-5, pp 21-28, 1999.

Brooke A., Kendrick.D, Meeraus.A and Raman.R, GAMS – A User's Guide", GAMS Development Corporation, 1217 Potomac Street, N.W. Washington, DC 20007, USA, http://www.gams.com/, 1998.

Camm, R.J. and Nuttall.P.M, Waste Minimization Incentive and Barriers, In A. Rossiter, Waste minimization through process design, Chapter 3, McGraw Hill publications, NY, 1995.

Chang, C.T. and Hwang.J.R, A Multiobjective programming approach to waste minimization in the utilities system of chemical processes, Chemical Engineering Science, Vol. 51, No. 16, pp. 3951-3965, 1996.

Cheng, L., Subrahmanian.E and Westerberg.A.W, Design and planning under uncertainty: issues on problem formulation and solution, Comp. Chem. Eng., 27(6), pp. 781-801, 2003.

Christ C., Integrated Environmental Protection Reduces Water Pollution, Chemical Engineering and Technology, Vol 22, No. 8, pp. 642-651, 1999.

Clift, R., Clean Technology-An introduction, J. Chem. Tech. Biotechnol, Vol. 62, pp. 321-326, 1995.

Cohen, Y. and Allen.D, An integrated approach to Process waste Minimization research. J. Of Hazardous Materials, 1992.

Comella, P.A. and Rittmeyer.R.W, Waste minimization/pollution prevention, Pollution Engineering, pp. 71-80, April 1990.

Crittenden, B.D. and Kolaczkowski S.T., Waste Minimization, A Practical Guide, Institution of Chemical Engineers, Rugby, UK, 1994.

Crittenden, B.D, Clean Technology , Section 2 & 3 , University of bath , Bath, 2001.

Dantus, M.M. and High.K.A, Economic Evaluation for the Retrofit of Chemical Processes through Waste Minimization and Process Integration, Ind. Eng. Chem. Res., Vol 35, No.12, pp. 4566-4578, 1996

Detchasit Prakotpol and Thongchai Srinophakun
GAPinch: genetic algorithm toolbox for water pinch technology, Chemical Engineering and Processing, Volume 43, Issue 2, pp. 203-217, February 2004.

Dolan, W.B., Cummings.P.T, and Le Van.M.D, Process optimization via simulated annealing: Application to network design, AICHE J., 35(5), pp. 725-736, 1989.

Doran G.F., Williams K.L, Drago J.A., Huang S.S., Leong L.Y.C., Converting oilfield product water to reusable quality, Journal of Petroleum Technology, Vol. 51, June 1999.

Douglas, J.M., Process synthesis for waste minimization, Ind. Eng. Chem. Res., Vol. 31, pp. 238-243, 1992.

Doyle .S.J and Smith .R Targeting water reuse with multiple contaminants Trans I ChemE Vol. 75, Part B, pp. 181 – 189, 1997.

Drabkin M., Fromm.C and Freeman.H.M, Development of Options for Minimising Hazardous Waste Generation, Environmental Progress, Vol. 7, No. 3, pp. 167-174, August 1988.

Duyvesteijn, C.P.T.M., Water Reuse in an Oil Refinery, Desalination, Vol. 119, pp. 357-358, 1998.

Edgar, T.F., Himmelblau.D.M, and Lasdon.L.S, Optimization of Chemical Processes, 2nd Ed., McGraw-Hill, NY, USA, 2001.

Edwards A.M.C., Johnston.N., Water and Wastewater Minimization – Aire and Clader Project, Journal of Chartered Institution of Water and Environmental Management, Vol. 10, No. 4, pp. 227-234, Aug. 1996.

El-Halwagi, M.M., and Manousiouthankis, V., Mass Exchanger Network, AICHE Journal, 35(8), 1989.

El-Halwagi, M.M., and Manousiouthankis, V.,Automatic Synthesis of Mass Exchanger Network with Single Component Target, CES 45(9), 1990.

El-Halwagi, M.M., Introduction to numerical optimization approach to pollution prevention, 1994.

El-Halwagi, M.M., Spriggs. H.D, Solve the design puzzles with mass integration. Chemical Engineering Progress, pp. 25-44, Aug. 1995.

El-Halwagi, M.M., Pollution Prevention Through Process Integration – Systematic Design Tools, Academic Press, California, USA, 1997.

Floudas, C.A. and Ciric.A.R Strategies for overcoming uncertainties in heat exchanger network synthesis, Comp. Chem. Engng., 13(10), pp. 113-1152, 1989.

Flower, J.R., Bikos.S.C, and Johnson.S.W, A modular approach to synthesis of cleaner process, Computers Chem. Engng., Suppl. pp. S45-S50, 1995.

Forstmeier.M, Goers.B and Wozny.G, Water network optimisation in the Process industry - case study of a liquid detergent plant , Journal of Cleaner Production, 2004.

Fromm C.H., Callahan.M.S, Freeman.H.M and Drabkin.M, Succeeding at waste minimization, Chemical Engineering, pp. 91-94, Sept. 14, 1987.

Galli, M. R., and Cerda.J, Synthesis of Flexible Heat Exchanger NetworksIII: Temperature and Flowrate Variations, Comp. Chem. Engng., 15(1), pp. 7-24, 1991.

Gunderson, Truls, A Process Integration Primer, SINTEF Energy Research, Norway, April 2002

Gerald Jodicke, Ultich Fischer, Konrad Hungerbuhler, Wastewater reuse: a new approach to screen for designs with minimal total costs, Computers & Chemical Engineering, Volume 25, 2001

Hallale, N. and Fraser.D.M, Super Targeting for Mass Exchange Networks, Trans. IChemE, Vol. 78, Part A, pp. 202-216, March 2000.

Herndon, D.M., Maling.M.J and Allen.J., Thirty Years of Industrial Wastewater Treatment, Pollution Engineering, Vol 31, 1999.

Hollod, G.J. and McCartney.R.F, Waste reduction in the chemical industry–Du Pont's approach, JAPCA, Vol. 38, No. 2, February 1988.

Hu. S , Chen.B and Shen.J, Non-convex Feasible Region of Heat Exchanger Networks with Uncertain Stream Parameters. Chin. J. Chem. Eng., 1(2), pp. 74-83, 1993.

Huang, Y.L. and Fan.L.T, Artificial Intelligence for waste minimization in the process industry, Computers in Industry, Vol. 22, pp. 117-128, 1993.

Huang C.H., Chang C.T. and Ling H.C, A mathematical model for water usage and treatment network design Ind Eng Chem, Vol. 38, No.7, pp. 2666 – 2679, 1999.

Jandrasi, F.J. and Masoomian.S.Z, Minimize Process Waste During Plant Design, Environmental Engineering World, pp. 6-15, Jan-Feb 1995.

Kallrath, J., Mixed Integer Optimization in the Chemical Process Industry. Experience, Potential and Future Perspective, Trans IChemE, Vol. 78, Part A, pp. 809-822, September 2000.

Kirsch, W., Muller.M.R, Annual Report for Industrial Assessment Center Program, Rutgers University Press, 1996.

Klee, H and Podar.M. Pollution Prevention in Petroleum Refining: The Amoco US EPA Project at Yorktown, AIChE Spring National Meeting, Paper #84b, Houston, Texas, April 1991.

Kosson D.S., Opportunities for Research in Hazardous Waste Minimization, Environmental Progress, Vol. 7, No. 3, August 1988.

Kuo, W-C.J., and Smith.R, Designing for the interactions between water-use and effluent treatment, Institution of Chemical Engineers pp. 287 - 301, March 1998.

Laing, I.G., Waste Minimization: The Role of Process Development, Chemistry & Industry, pp. 682-686, 21 September 1992.

Lewin, D.R. A generalized method for HEN synthesis using stochastic optimization –II. The synthesis of cost-optimal networks, Comp. Chem. Eng., 22(10), pp. 1387-1405, 1998.

Lewin, D.R., Wang.H, and Shalev.O, A generalized method for HEN synthesis using stochastic optimization –I, General framework and MER optimal synthesis, Comp. Chem. Eng., 22(10), pp. 1503-1513, 1998.

Linhoff, B., et al., A User guide on Process Integration for the Efficient Use of Energy, Revised 1st Ed., Institution of Chemical Engineers, Rugby, U.K., 1994.

Linhoff, B., and Smith.R, Recent Development in Pinch Analysis, Paper presented at Process System Engineering, Kyonju, Korea, 1994.

Linniger, A.A., Chakraborty.A, and Colberg.R.D, Planning of Waste Reduction Strategies under Uncertainty, Computers and Chemical Engineering, Vol 24, 2000.

Lie, Y.A., Bruce Lucas and James Mann, Up-to-Date tools for Water System Optimization, Chemical Engineering, pp. 30 – 41, January 2004.

Mann, J.G., and Liu Y.A. Industrial water reuse and wastewater minimization, Chapter 9, McGraw-Hill Professional Engineering, 11 West 19 Street, NY 10011, 1999.

Mata, T.M. and Costa.C.A.V, Application of life cycle assessment and sustainable process index to process design, University of Porta, 2000

Maunder, A., How much does waste really cost you? Environmental Management journal, pp. 71-74, April 1999.

Mitchell-Fox, D. Legal Aspects of Pollution Prevention, In A. Rossiter, Waste minimization through process design, Chapter 2, McGraw Hill publications, NY, 1995.

Morse, J.S., Khan.J.A, Caldwell.M, Baxter.S, Veludhandi.K, Drake.B.D, and Smith.R.L, Jr, A Unit Operation Approach to Waste Minimization, Journal of Environment Science and Health, Vol. A29, No. 7, pp. 1471-1489, 1994.

Mulholland, K. L and Dyer.J, Process Analysis via Waste Minimization: Using Dupont's Methodology to Identify Process Improvement Opportunities, Environmental Progress, Vol. 20, No. 2, July 2001.

Murty, M.N. and Kumar.S, Measuring Cost of Environmentally Sustainable Industrial Development in India: A Distance Function Approach, Revised, December, 2000.

Nelson, K.E., Finding Process improvements–The Six Places to Look, Energy Engineering, Vol. 96, No.1, pp 61-66, 1999.

Nielsen, J.S., Hansen.M.W, and. Kristensen.K.P, Retrofit and optimization of industrial heat exchanger networks: A complete benchmark problem, Comp. Chem. Eng., 21(Suppl.), pp. S469-S474, 1997.

Nobel, C.E., and Allen D.T, Using Geographic Information System (GIS) in Industrial Water Reuse Modelling, Trans. IChemE, Vol. 78, Part B, pp. 295-303, July 2000.

Oliver, J.J., Pollution prevention Or Pollution Control, In A. Rossiter, Waste minimization through process design, Chapter 1, McGraw Hill publications, 1995.

Papalexandri K.P., Pistikopoules.E.N and Floudas.C.A, Synthesis of mass exchanger networks for the waste minimization: An MINLP approach, IChemE Symposium Series no.133, pp. 351-358, 1994.

Rice, S.C., Minimising Waste from R&D Activities, Chemical Engineering, pp. 85-88, October 24, 1988.

Roberge, H.D., Sikora.R.P and Baetz.B.W, Use of optimization modelling to evaluate industrial waste reduction options: Application to a sour gas plant, Waste Management, Vol. 14, No. 7, pp. 649-654, 1994.

Ross B. and Sasser.M, Reduce, Reuse, Recycle: Water Conservation and Industry, Consulting-Specifying Engineer, pp. 60-64, October 1998.

Rossiter, A.P., et al., Reduce Process Emissions at Source Using Pinch Analysis, AIChE Second Topical Conference on Pollution Prevention, Pittsburgh, PA, August 1991.

Rossiter, A.P., Spriggs.D and Klee.H Jr., Apply Process Integration to Waste Minimization, Chemical Engineering Progress, January 1993.

Rossiter, A.P. and Nath.R, , Wastewater Minimization using Nonlinear Programming, In A. Rossiter, Waste minimization through process design, Chapter 17, McGraw Hill publications, 1995.

Savulescu .L.E, Sorin.M and Smith.R ,Direct and indirect heat transfer in water network systems, Applied Thermal Engineering, Volume 22, Issue 8, pp. 981-988, June 2002.

Smith, R., State of the art in process integration, Applied Thermal Engineering, Volume 20, Issues 15-16, , pp. 1337-1345, 1 October 2000.

Smith, R., Wastewater minimization, Rossiter, Waste minimization through process design, Chapter 8, McGraw Hill publications, NY, 1995.

Smith, R. and Petela, E, Waste minimization in the process industries, Part 1: The problem, The Chemical Engineer, 31 October 1991.

Shapiro J.F. Modeling the supply chain, Duxbury Thomson Learning Inc., Duxbury, Pacific Grove, CA 93950 USA, (ISBN 0-534-37363-1), 2001.

Superfund Amendments and Reauthorization Acts (SARA), http://www4.law.cornell.edu/uscode/42/ch103.html, 1986.

Suriyapraphadilok, U., Network prototype of water-wastewater management, Master of Engineering Thesis, Chemical Engineering Practice School, King Monkut's University of Technology Thonburi, 1998.

Tainsh, R.A. and Rudman, A.R., Practical techniques and methods to develop an efficient water management strategy, Paper presented at: IQPC Conference, Water Recycling and Efficient Re-Use, 26th/27th April, 1999.

Takama, N., Kuriyama, T., Shiroko, K., and Umeda, T., Optimal Water Allocation in a Petroleum Refinery, PACHEC, Denver, 1977.

Terras, C. Vandevivere.P, Verstraete.W, Optimal Treatment and Rational Reuse of Water in Textile Industry, Water Science Technology, Vol. 39, No.5, pp. 81-88, 1999.

Ullmer.C, Kundeb.N, Lassahnc.A, Gruhn.G and Schulzb.K, WADO™: water design optimization - methodology and software for the synthesis of process water systems, Journal of Cleaner Production, 2003.

Underwood, J.D., Source reduction: A Waste Solution, Chemistry & Industry, 3 Jan. 1994.

US EPA, Profile of the Petroleum Refining Industry, Office of Enforcement and Compliance Assurance, Sept. 1995.

US EPA, U.S Environmental Protection Agency, Office of Research and Development, Washington DC, Pollution Prevention Research Plan. Report to congress, March, 1990.

Wilson D.C., Stick or Carrot?: The use of policy measures to move waste management up the hierarchy, Waste Management & Research, Vol. 14, pp. 385-398 , 1996.

Wang,Y.P., & Smith, R., Wastewater Minimization, Chemical Engineering Science, Vol. 49, No.7, pp. 981 – 1006, 1994.

Wang Bin, Feng Xiao and Zhang Zaoxiao, A design methodology for multiple-contaminant water networks with single internal water main, Computers & Chemical Engineering, Volume 27, Issue 7, 15 July 2003.

Zadorsky, W.M., Cleaner production as a base of sustainable product development, Pridneprovie Cleaner production Centre, Ukrainian State University of Chemical technology, http://www.environmental-center.com, 1999.

Zbontar L., and Glavic.P, Total site: Wastewater Minimization – Wastewater Reuse and Regeneration Reuse, Resources, Conservation and Recycling, Vol. 30, No.4, pp. 261-275, 2000.

APPENDIX A

A. OVERVIEW OF PETROLEUM REFINING PROCESSES

A.1. Basis of Crude Oil

The first commercial oil well was drilled in 1859 and the first refinery was opened two years later. Refining is the processing of one complex mixture of hydrocarbons into a number of other complex mixtures of hydrocarbons. The safe and orderly processing of crude oil into flammable gases and liquids at high temperatures and pressures using vessels, equipment, and piping subjected to stress and corrosion requires considerable knowledge, control, and expertise. The refining process rearranges the structures and bonding patterns of hydrocarbons in the crude oil into different hydrocarbon molecules and compounds.

Crude oils are complex mixtures containing many different hydrocarbon compounds that vary in appearance and composition from one oil field to another. Crude oils range in consistency from water to tar-like solids, and in colour from clear to black.

An "average" crude oil contains about 84% carbon, 14% hydrogen, 1-3% sulphur, and less than 1% each of nitrogen, oxygen, metals, and salts. Crude oils are generally classified as paraffinic, naphthenic, or aromatic, based on the predominant proportion of similar hydrocarbon molecules. Crude oils that contain appreciable quantities of hydrogen sulphide or other reactive sulphur compounds are called "sour." Those with less sulphur are called "sweet."

A.2. Major Refinery Products

Major products from a typical refinery include: Liquefied Petroleum Gas (LPG), gasoline, kerosene, distillate fuels, residual fuels, coke and asphalt, solvents (such as benzene, toluene, and xylene), petrochemicals (such as ethylene, propylene, butylenes, isobutylene, etc.) and lubricants (including motor oils, industrial greases, lubricants, cutting oils etc.).

A.3. Petroleum Refining Operations

Petroleum refining begins with the distillation, or fractionation, of crude oils into separate hydrocarbon groups. Most distillation products are further converted into more usable products by changing the size and structure of the hydrocarbon molecules through cracking, reforming, and other conversion processes as will be discussed later. These converted products are then subjected to various treatment and separation processes to remove undesirable constituents and improve product quality.

A simplified process flow sheet of a typical refinery is shown in Figure A.1. A brief description of major refining processes will be given in the following paragraphs.

A.3.1. Crude Oil Pre-Treatment (Desalting)

Crude oil often contains water, inorganic salts, suspended solids, and water-soluble trace metals. As a first step in the refining process, to reduce corrosion, plugging, and fouling of equipment and to prevent poisoning the catalysts in processing units, these contaminants must be removed by desalting (dehydration).

The feedstock crude oil is heated to between 150°F and 350°F to reduce its viscosity and surface tension for easier mixing and separation of the water. In both methods other chemicals may be added. Ammonia is often used to reduce corrosion. Caustic or acid may be added to adjust the pH of the water wash. Wastewater and contaminants are discharged from the bottom of the settling tank to the wastewater treatment facility. The desalted crude is continuously drawn from the top of the settling tanks and sent to the crude distillation (fractionating) tower.

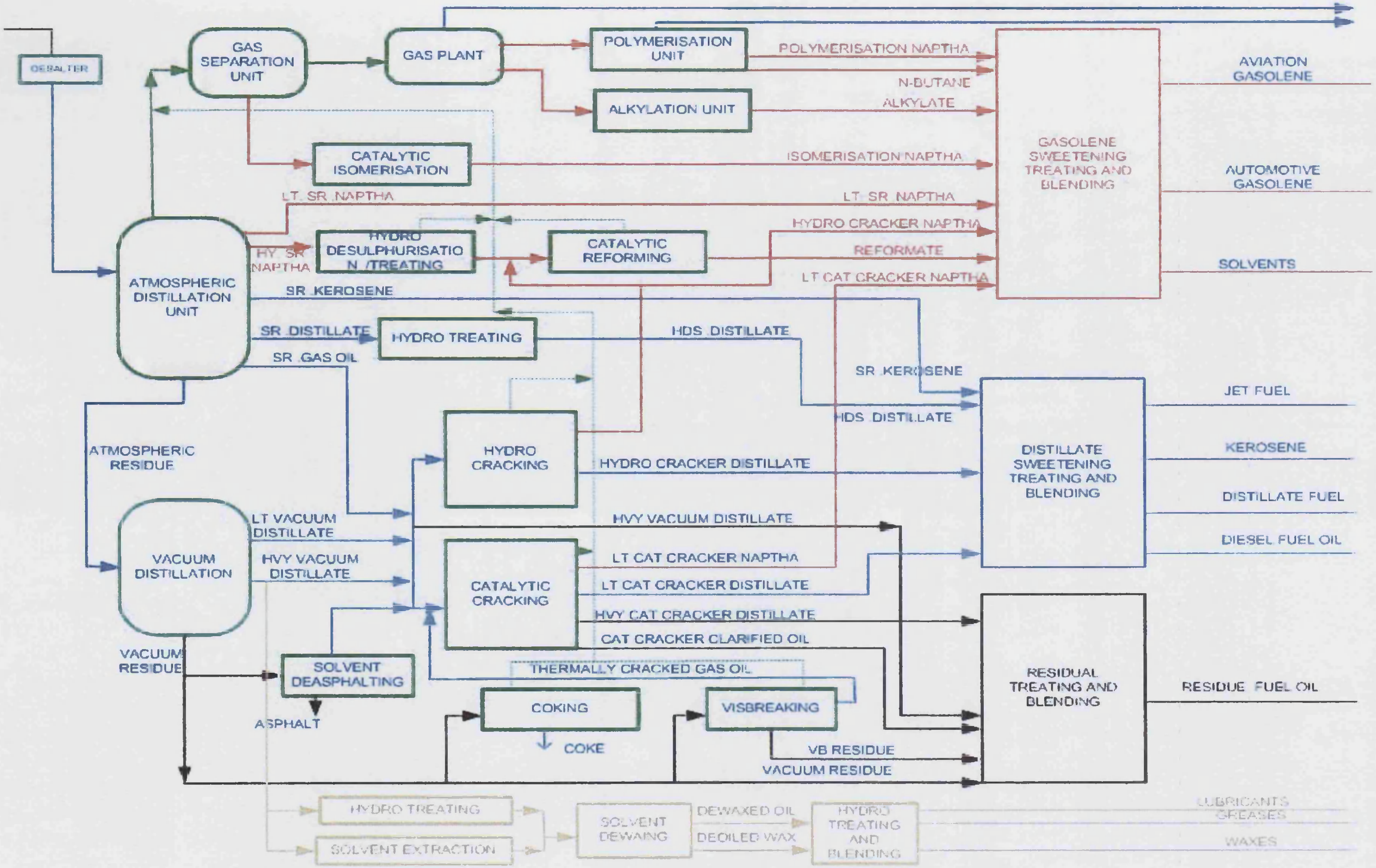


Figure A.1: Simplified Refinery Process Flow sheet

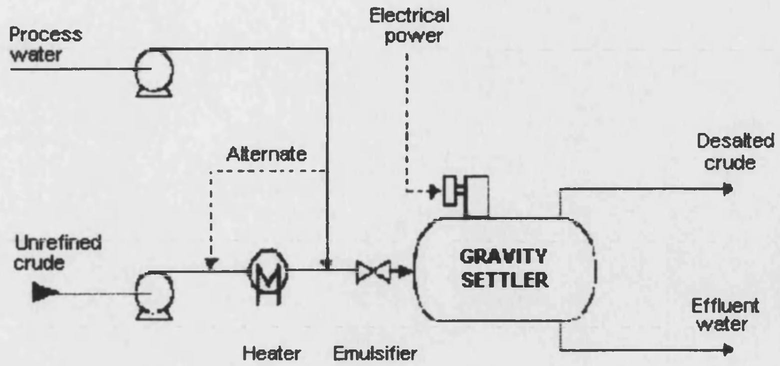


Figure A.2: Electrostatic Desalting Process

A.3.1.1. Sour Water from Desalting Units

Water is used for washing the crude to remove salts. Depending on the type of crude feedstock and the treatment chemicals used, the wastewater will contain varying amounts of chlorides, sulphides, bicarbonates, ammonia, hydrocarbons, phenol, and suspended solids.

A.3.2. Crude Oil Distillation (Fractionation)

The first step in the refining process is the separation of crude oil into various fractions or straight-run cuts by distillation in atmospheric and vacuum towers.

A.3.2.1. Atmospheric Distillation

The desalted crude feedstock is preheated using recovered process heat. The feedstock then flows to a direct-fired crude charge heater where it is fed into the vertical distillation column just above the bottom, at pressures slightly above atmospheric and at temperatures ranging from 650°F to 700° F (heating crude oil above these temperatures may cause undesirable thermal cracking). All but the heaviest fractions flash into vapour. As the hot vapour rises in the tower, its temperature is reduced. Heavy fuel oil or asphalt residue is taken from the bottom. At successively higher points in the tower, the various major products including lubricating oil, heating oil, kerosene, gasoline, and uncondensed gases (which condense at lower temperatures) are drawn off.

The distillation process separates the major constituents of crude oil into so-called straight-run products. The heavy residue that is left behind in atmospheric distillation is often distilled further under high vacuum.

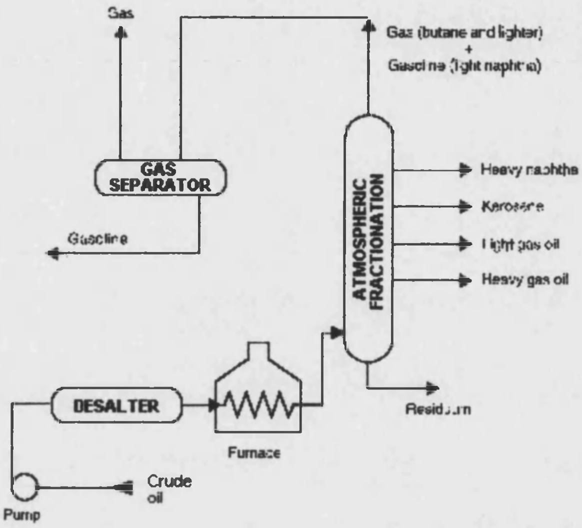


Figure A.3: Atmospheric Distillation Unit

A.3.2.2. Vacuum Distillation

In order to further distil the residuum or topped crude from the atmospheric tower at higher temperatures, reduced pressure is required to prevent thermal cracking. The process takes place in one or more vacuum distillation towers. The principles of vacuum distillation resemble those of fractional distillation and, except that larger-diameter columns are used to maintain comparable vapour velocities at the reduced pressures, the equipment is also similar. A typical first-phase vacuum tower may produce gas oils, lubricating-oil base stocks, and heavy residual for propane deasphalting. A second-phase tower operating at lower vacuum may distil surplus residuum from the atmospheric tower, which is not used for lube-stock processing, and surplus residuum from the first vacuum tower not used for deasphalting. Vacuum towers are typically used to separate catalytic cracking feedstock from surplus residuum.

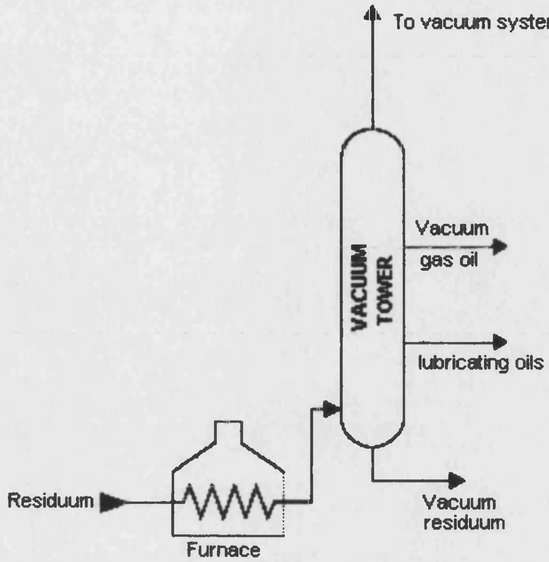


Figure A.4: Vacuum Distillation Unit

A.3.2.3. Sour Water from Fractionation Towers

In both atmospheric and vacuum distillation columns, steam is used for stripping and chemicals are used to control corrosion by hydrochloric acid that is produced in fractionation towers during distillation. Ammonia may be injected into the overhead stream prior to initial condensation and/or an alkaline solution may be carefully injected into the hot crude-oil feed. Wash water is also used to remove the salt in the overhead condensers. If sufficient wash-water is not injected, deposits of ammonium chloride can form and cause serious corrosion. In vacuum column, steam is used as motive force for ejectors. All these water end up as sour water and to sour water treatment unit.

A.3.3. Coking Process

Coking is a severe method of thermal cracking used to upgrade heavy residuals into lighter products or distillates. Coking produces straight-run gasoline (coker naphtha) and various middle-distillate fractions used as catalytic cracking feedstock. The process reduces hydrogen content of the residue in a form of carbon called "coke." The two most common processes are delayed coking and continuous (contact or fluid) coking. Three typical types of coke are obtained (sponge coke, honeycomb coke, and needle coke) depending upon the reaction mechanism, time, temperature, and the crude feedstock.

Depending upon the process employed to treat the heavy residue, the coking process can be classified in to delayed Coking and Continuous coking.

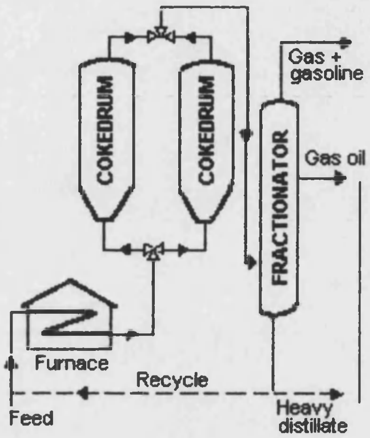


Figure A.5: Delayed Coking

A.3.3.1. Wastewater from Coking Units

Water is used for coke cutting and steam stripping which results as sour water. Wastewater generated from coking processes may be highly alkaline and contain oil, sulphides, ammonia, and/or phenol.

A.3.4. Catalytic Cracking

Catalytic cracking is similar to thermal cracking except that catalysts facilitate the conversion of the heavier molecules into lighter products. Catalytic cracking breaks complex hydrocarbons into simpler molecules in order to increase the quality and quantity of lighter, more desirable products and decrease the amount of residuals.

There are three basic functions in the catalytic cracking process:

a) Reaction: Feedstock reacts with catalyst and cracks into different hydrocarbons.

b) Regeneration: Catalyst is reactivated by burning off coke.

c) Fractionation: Cracked hydrocarbon stream is separated into various products.

A.3.4.1. Fluid Catalytic Cracking (FCC)

The most common catalytic cracking process is FCC (Fluid Catalytic Cracking), in which the oil is cracked in the presence of a finely divided catalyst which is maintained in an aerated or fluidised state by the oil vapours. The fluid cracker consists of a catalyst section and a fractionating section that operate together as an integrated processing unit. The fluid catalyst is continuously circulated between the reactor and the regenerator using air, oil vapours, and steam as the conveying media.

The vapour from reactor section (cracked products) is then charged to a fractionating column where it is separated into fractions, and some of the heavy oil is recycled to the riser. Spent catalyst is regenerated to get rid of coke. Fresh catalyst is added and worn-out catalyst removed to optimize the cracking process.

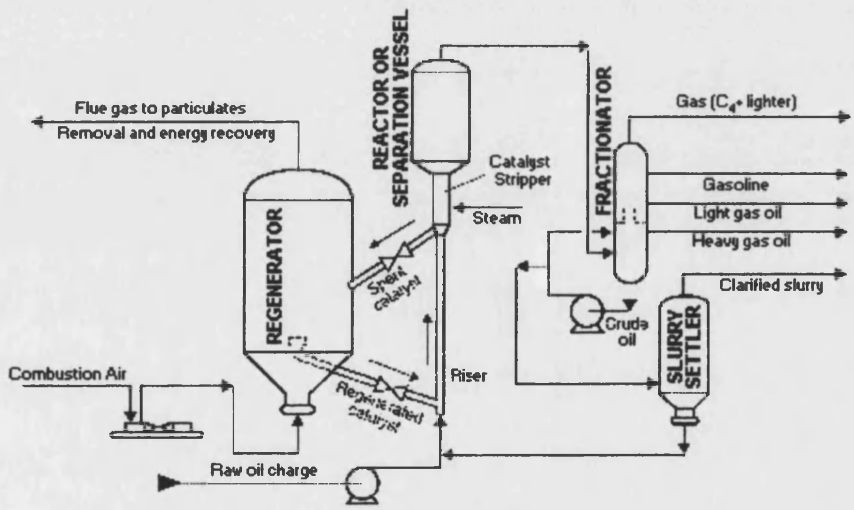


Figure A.6: Fluid Catalytic Cracking Unit

A.3.4.2. Wastewater from Catalytic Cracking Units

Steam is used as stripping medium in FCC and this gets condensed in the overhead system of FCC. Water is also used for washing fluids (to remove salts) in overhead exchangers. These two water results in generation of sour water. When processing high-nitrogen feedstock, exposure to ammonia and cyanide may occur, subjecting carbon steel equipment in the FCC overhead system to corrosion, cracking, or hydrogen blistering.

These effects may be minimized by water wash or corrosion inhibitors. Water wash may also be used to protect overhead condensers in the main column subjected to fouling from ammonium hydrosulphide. Inspections should include checking for leaks due to erosion or other malfunctions such as catalyst build-up on the expanders, coking in the overhead feeder lines from feedstock residues, and other unusual operating conditions. The wash water removes the contaminants in the system and becomes sour water, which is then sent for treatment.

A.3.5. Hydrocracking

Hydrocracking is a two-stage process combining catalytic cracking and hydrogenation, wherein heavier feed stocks are cracked in the presence of hydrogen to produce more desirable products. The process employs high pressure and temperature, over a catalyst, and in the presence hydrogen.

Hydrocracking produces relatively large amounts of isobutane for alkylation feedstock. Hydrocracking also performs isomerization for pour-point control and smoke-point control, both of which are important in high-quality jet fuel.

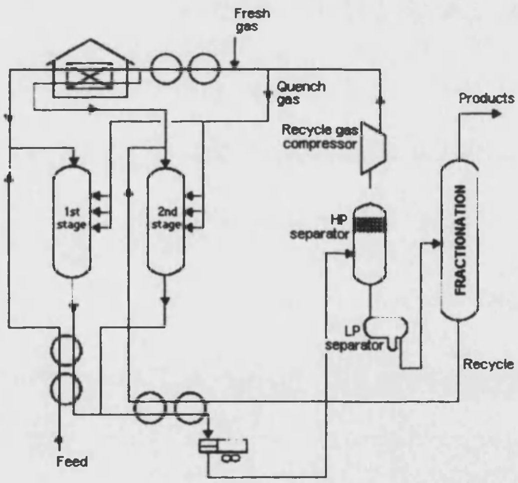


Figure A.7: Hydro Cracking Unit

The liquid effluent from the reactor is charged to a fractionator and desired products are separated. The fractionator bottoms are again mixed with a hydrogen stream and charged to the second stage. Like the out turn of the first stage, the second stage product is separated from the hydrogen and charged to the fractionator.

A.3.5.1. Wastewater from Hydrocracking Unit

Wash water used in exchangers and stripping steam used in distillation column are the main source of wastewater. When processing high-nitrogen feedstock, the ammonia and hydrogen sulphide form ammonium hydrosulphide, which causes serious corrosion at temperatures below the water dew point. Ammonium hydrosulphide is also present in sour water stripping. Catalyst steam stripping and regeneration create waste streams containing sour water and ammonia.

A.3.6. Catalytic Reforming

Catalytic reforming is an important process used to convert low-octane naphtha into high-octane gasoline blending components called reformate. Depending on the properties of the naphtha feedstock (as measured by the paraffin, olefin, naphthene, and aromatic content) and catalysts used, reformates can be produced with very high concentrations of toluene, benzene, xylene, and other aromatics useful in gasoline blending and petrochemical processing. Hydrogen, a significant by-product, is separated from the reformate for recycling and use in other processes.

The first step is preparation of the naphtha feed to remove impurities and reduce catalyst degradation. The naphtha feedstock is then mixed with hydrogen, vaporized, and passed through a series of alternating furnace and fixed-bed reactors containing a platinum catalyst. The effluent from the last reactor is cooled and sent to a separator to permit removal of the hydrogen-rich gas stream from the top of the separator for recycling. The liquid product from the bottom of the separator is sent to a fractionator called a stabilizer (butanizer). It makes a bottom product called reformate; butanes and lighter go overhead and are sent to the saturated gas plant

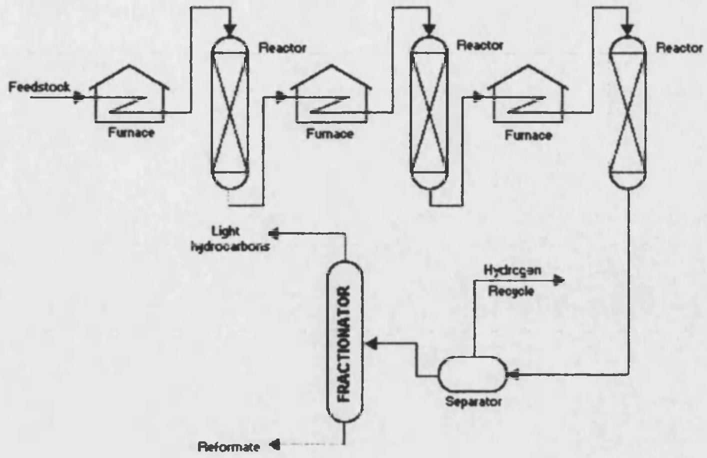


Figure A.8: Platforming Unit

A.3.6.1. Wastewater from Catalytic Reforming Unit

Water wash should be considered where stabilizer fouling has occurred due to the formation of ammonium chloride and iron salts. Ammonium chloride may form in pre-heat exchangers and cause corrosion and fouling. However, the effect due to ammonium chloride can be minimized by water wash, which ultimately results in sour water generation. Hydrogen chloride from the hydrogenation of chlorine compounds may form acid or ammonium chloride salt.

A.3.7. Catalytic Hydrodesulphurization

Catalytic hydrodesulphurization is a hydrogenation process used to remove about 90% of contaminants such as nitrogen, sulphur, oxygen, and metals from liquid petroleum fractions. These contaminants, if not removed from the petroleum fractions, can have detrimental effects on the equipment, the catalysts, and the quality of the finished product. Typically, hydrodesulphurization is done prior to processes such as catalytic reforming so that the catalyst is not contaminated by untreated feedstock. Hydrodesulphurization is also used prior to catalytic cracking to reduce sulphur and improve product yields, and to upgrade middle-distillate petroleum fractions into finished kerosene, diesel fuel, and heating fuel oils.

A.3.7.1. Catalytic Hydro desulphurization Process

Hydro desulphurization for sulphur removal is called hydrodesulphurisation. In a typical catalytic hydrodesulphurisation unit, the feedstock is deaerated and mixed with hydrogen, preheated in a fired heater (600°F to 800° F) and then charged under pressure (up to 1,000 psi) through a fixed-bed catalytic reactor. In the reactor, the sulphur and nitrogen compounds in the feedstock are converted into H_2S and NH_3, respectively.

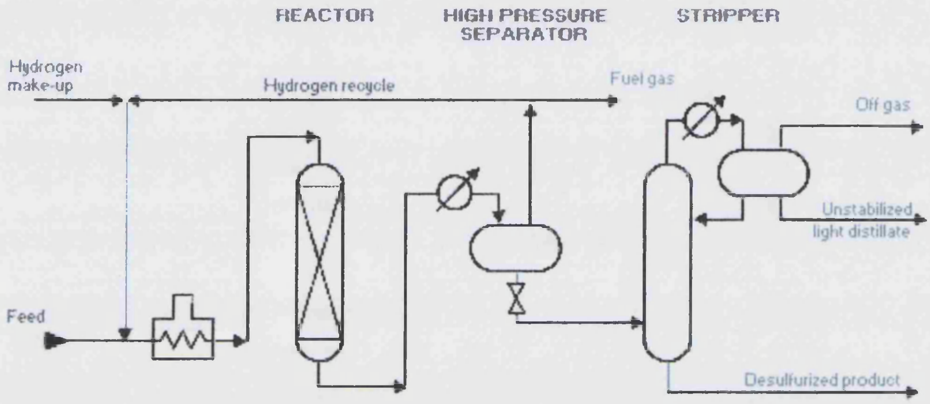


Figure A.9: Distillate Hydrodesulphurization Unit

The reaction products are cooled and fed to a liquid/gas separator. The hydrogen-rich gas from the high-pressure separation is recycled to combine with the feedstock, and the low-pressure gas stream rich in H_2S is sent to a gas-treating unit where H_2S is removed. The clean gas is then suitable as fuel for the refinery furnaces. The liquid stream is the product from hydrodesulphurization and is normally sent to a stripping column for removal of H_2S and other undesirable components. Hydrodesulfurized products are blended or used as catalytic reforming feedstock.

A.3.7.2. Wastewater from Catalytic Hydrodesulphurization Units

The steam stripping of desulphurized products causes generation of sour water, which has to be treated separately before disposal or reuse. Ejector steam also results in generation of sour water.

APPENDIX B

B. SELECTED GAMS FILES

1. EXAMPLE -1	INPUT	FILE	3 PAGES.
	OUTPUT	SUMMARY	2 PAGES.
2. CASE-3 (DETERMINISTIC MODEL)			
	INPUT	FILE	9 PAGES.
	OUTPUT	SUMMARY	3 PAGES

```
*INDUSTRIAL WATER REUSE AND WASTEWATER MINIMIZATION
* WITH A WATER LOSS THROUGH MATHEMATICAL OPTIMIZATION
* UPDATED  ON  12/12/04
* LITERATURE EXAMPLE 1  IN CHAPTER  5  WITH  NO REGENERATOR
* THIS  PROGRAM IS UPDATED  BASED ON   WANG AND SMITH PAPER
*  WASTE WATER  MINIMISATION CHEMICAL ENGG SCIENCE  1994



SETS
*UNITS
* STEAM STRIPPER (CDU), OPS1, HYDRO DESULPHURISER (OPS2), DESALTER (OPS3)
I UNITS  /OPS1, OPS2, OPS3/
* IMPURITIES PRESENT IN THE SOUR WATER
M IMPURITIES /H2S,NH3,CL2/
ALIAS(I,N);
execute "gams transdata r=s1"
PARAMETERS

*COST Factors
FWCOST FRESH WATER PRICE   /0.6/
WTCOST WASTE WATER PRICE  /1/
RUCOST REUSE WATER PRICE   /.05/

* TOTAL WATER USED IN THE PROCESS ( FRESH WATER + STEAM + REGEN-REUSE + REUSE)
TW(I) LIMITING  WATER FLOW AS PER PROCESS REQU  IN T PER HR /OPS1 45, OPS2 34,
OPS3 56/

*TOTAL STEAM FLOW TO UNIT
ST(I) STEAM FLOW /OPS1 45,OPS2 0,OPS3 0/


* MAXIMUM IMPURITIES AT THE OUTLET   FOR EACH PROCESS AS PER LICENSOR AS PER
DESIGN
TABLE CMAXIN(I,M) limiting the inlet concentrations
            H2S    NH3   CL2
  ops1        0      0     0
  OPS2       20     300    45
  OPS3      120      20   200;



* MAXIMUM IMPURITIES AT THE OUTLET   FOR EACH PROCESS AS PER LICENSOR AS PER
DESIGN
TABLE COUT1(I,M) outlet concentrations
            H2S    NH3     CL2
  OPS1       15     400    35
  OPS2      120    12500   180
  OPS3      220     45     9500;

* MAXIMUM IMPURITIES AT THE OUTLET   FOR EACH PROCESS AS PER LICENSOR AS PER
DESIGN
TABLE DELTAM1(I,M) MASS LOAD
            H2S    NH3     CL2
  OPS1      0.675  18.0    1.575
  OPS2      3.4    414.8   4.59
  OPS3      5.6    1.4     520.8;
```

```
PARAMETERS FWB Fresh water flowrate to boiler in T per hr;
           FWB = sum(i, ST(i))*1.00;
PARAMETERS DELTAM(I,M);
           DELTAM(I,M)=DELTAM1(I,M)*1.00;

VARIABLES
COST         Total cost  per year
FW(I)        Flowrate of freshwater to unit i in T per hr
REUSE(I,N)   Flowrate of water reuse from unit i to unit n in T per hr
CIN(I,M)     Inlet concentration of contaminant m to unit i in ppm
FWTOT        Total freshwater demand in T per hr
WWFLOW       Total wastewater flowrate to water treatment and disposal in T per hr
REUSETOT     Total wastewater reused in T per hr
FT(I)        Wastewater flowrate from unit i to treatment and disposal in T per hr
COUT(I,M)

POSITIVE VARIABLE FW, REUSE, CIN,     FT, cmaxout1;
POSITIVE VARIABLE FWTOT,  WWFLOW, REUSETOT;
****************************


REUSE.up('OPS3','OPS1')=0;
FW.LO('OPS1')= 0;
FW.LO('OPS2')= .01;
FW.LO('OPS3')= .1;
FW.UP('OPS1')= 60;
FW.UP('OPS2')= 40;
FW.UP('OPS3')= 60;



EQUATIONS
         OBJFUN          Objective function
         REUSESAME(I)    Reuse from the same unit is not allowed
         CINLET(N,M)     Inlet concentration
         CINCONS(N,M)    Inlet concentration constraint
         COUTLET(N,M)    Outlet concentration
         COUTCONS(N,M)    Inlet concentration constraint
         MASSBAL(N)      Mass balance for a water using unit
         FRESHWATER      Total freshwater demand
         REUSET          Total reused water between units
         SUMWASTE        Total wastewater to treatment and disposal
         const1;




* Cost function
OBJFUN  ..  COST =E= (FWCOST*FWTOT + WTCOST*(WWFLOW) + RUCOST*REUSETOT)*24*365;;

* No reuse directly from the same unit
REUSESAME(I) .. REUSE(I,I) =E= 0;

* Forbidding  reuse  from desalter to OPS2
```

```
const1 .. REUSE('OPS3','OPS2') =E= 0;


* Inlet impurities concentration and constraint on unit N
CINLET(N,M)  ..  CIN(N,M)*(FW(N)+sum(i, REUSE(i,N))) =E= sum(i, REUSE(i,N)*COUT(i
M));
CINCONS(N,M) ..  CIN(N,M) =L= CMAXIN(N,M);

* Outlet impurities constraint on unit N
COUTLET(N,M) ..  (FW(N)+ST(N)+ sum(i, REUSE(i,N)) )*(COUT(N,M)-CIN(N,M)) =E=1000*
1.*DELTAM(N,M);
COUTCONS(N,M)..  COUT(N,M) =L= COUT1(N,M);

* Material balance for water using unit
MASSBAL(N)    ..  FW(N)+ST(N)+ sum(i, REUSE(i,N)) - sum(i, REUSE(N,i))  - FT(N) =E
0;


* Total freshwater demand
FRESHWATER    ..  FWTOT =E= sum(i, FW(i)) + FWB;

* Total reused water
REUSET        ..  REUSETOT =E= sum(i, sum(n, REUSE(i,n)));

* Total Wastewater to treatment and disposal unit
SUMWASTE      ..  WWFLOW =E= sum(i, FT(i))  + 0.00*FWB/1.03;

MODEL SUPER / ALL/;
OPTION ITERLIM = 1000000;
*OPTION NLP = MINOS;
SOLVE SUPER USING NLP MINIMIZING COST;
DISPLAY COST.L, FW.L, REUSE.L, CIN.L, cout.l,cout1,  FWTOT.L,
WWFLOW.L, REUSETOT.L,deltam,  FT.L;
```

```
GAMS Rev 130  Windows NT/95/98                    07/02/05 15:12:20  PAGE      6
G e n e r a l   A l g e b r a i c   M o d e l i n g   S y s t e m
E x e c u t i o n


----    139 VARIABLE  COST.L                  =  1493302.122  Total cost  per year


----    139 VARIABLE  FW.L  Flowrate of freshwater to unit i in T per hr

OPS2  8.500,    OPS3 52.162


----    139 VARIABLE  REUSE.L  Flowrate of water reuse from unit i to unit n in
                               T per hr

            OPS2        OPS3

OPS1      25.500       2.668


----    139 VARIABLE  CIN.L  Inlet concentration of contaminant m to unit i in
                             ppm

             H2S         NH3          CL2

OPS2      11.250     300.000       26.250
OPS3       0.730      19.467        1.703


----    139 VARIABLE  COUT.L

             H2S         NH3          CL2

OPS1      15.000     400.000       35.000
OPS2     111.250   12500.000      161.250
OPS3     102.862      45.000     9500.000


----    139 PARAMETER COUT1  outlet concentrations

             H2S         NH3          CL2

OPS1      15.000     400.000       35.000
OPS2     120.000   12500.000      180.000
OPS3     220.000      45.000     9500.000


----    139 VARIABLE  FWTOT.L                 =      105.662  Total freshwater
                                                              demand in T per hr
            VARIABLE  WWFLOW.L                =      105.662  Total wastewater
                                                              flowrate to water
                                                              treatment and
                                                              disposal in T per hr
            VARIABLE  REUSETOT.L              =       28.168  Total wastewater
                                                              reused in T per hr

```

```

----     139 PARAMETER DELTAM

              H2S         NH3         CL2

OPS1        0.675      18.000       1.575
OPS2        3.400     414.800       4.590
OPS3        5.600       1.400     520.800


----     139 VARIABLE  FT.L  Wastewater flowrate from unit i to treatment and
                             disposal in T per hr

OPS1 16.832,    OPS2 34.000,    OPS3 54.831


EXECUTION TIME       =        0.047 SECONDS    1.6 Mb      WIN205-130


USER: Dr. Haitham Lababidi                               G020403:1117AP-WIN
      Kuwait University, Chemical Engineering Department         DC3752

**** FILE SUMMARY

INPUT      E:\SAR\PHD\GAMSFILES\EXAMPLE 1 FOR REPORT.GMS
```

```
* INDUSTRIAL WATER REUSE AND WASTEWATER MINIMIZATION
* WITH A WATER LOSS THROUGH MATHEMATICAL OPTIMIZATION
* FIRST DEVELOPED  ON 01/07/2002
* LAST UPDATE 10/12/2004
* PREPARED BY SUAD
* CASE-3 IS BASED   ON  FIXED  OUTLET  CONCENTRATION.
* IT IS REGEN-REUSE CASE AND RESUE CASE

SETS
*UNITS  CONSIDERED
I UNITS  /CDU, ARD, VRU,TGT ,KD, GOD, HCR, DESAL, FCC/

* IMPURITIES PRESENT IN THE SOUR WATER
M IMPURITIES /H2S,NH3,CL2,HCN/

* PROCESS PARAMETERS WILL AFFECT  SOUR WATER PRODUCTION QUANTITY / QUALITY
L PROCESS PARAMETERs / PRESSURE , TEMP , CAPACITY/
ALIAS(I,N);

execute "gams transdata r=s1"
PARAMETERS
*LIMIT FOR DESALTER  BASED ON MASS LOAD CHANGE
DSLIMIT MASSLOAD /26484/

*REGENERATED WATER QUALITIES
CRMINOUT(M)   REGENERATOR OUTLET CONCENTRATION IN PPM /H2S 10,NH3 10,CL2 10,HCN 0
/

*COST FACTORS KD/M3
FWCOST FRESH WATER PRICE kdperm3  /0.6/
RWCOST REGEN WATER PRICE kdperm3  /0.1/
WTCOST WASTE WATER PRICE kdperm3  /1/
RUCOST REUSE WATER PRICE kdperm3  /.05/

* TOTAL WATER USED IN THE PROCESS ( FRESH WATER + STEAM + REGEN-REUSE + REUSE)
TW(I) TOTAL WATER FLOW AS PER PROCESS REQU  IN TONS PER HOUR /CDU 53.5, ARD 68.9,
VRU 45.35, TGT 27.2, KD  4.5, GOD 14.9, HCR  17.2, DESAL 90.7,FCC  18.1 /

*TOTAL STEAM FLOW TO UNIT


ST(I) STEAM FLOW /CDU 52.5,ARD 0.5,VRU 45.35,TGT 27.2,KD 1.8,GOD 6.5,HCR 1,DESAL
0.1, FCC 4.5/

* MAXIMUM ALLOWABLE IMPURITIES AT THE INLET  FOR EACH PROCESS AS PER LICENSOR
TABLE CMAXIN(I,M) Maximum allowable  inlet concentrations
           H2S    NH3  CL2  HCN
  CDU       80     80  10    0
  ard       50    200  10    0
  vru       50     50  10    0
  tgt       80    200  10    0
  kd       100    100  10    0
  god      100    100  10    0
  hcr      100    200  10    0
  desal     20     50  10    0
  fcc       10    100  20    0 ;
```

```
* TYPICAL IMPURITIES AT THE OUTLET   FOR EACH PROCESS AS PER LICENSOR AS PER
DESIGN
TABLE COUT1(I,M) outlet concentrations
              H2S     NH3    CL2     HCN
  CDU          80     200     10       0
  ard       41000   20700     10       0
  vru          80      70     10       0
  tgt        1500     700     10       0
  kd          400     200     10       0
  god        3600     800     10       0
  hcr       25060   12530     10       0
  desal        10     100    300       2
  fcc        3000     300     40     100;

TABLE PROCESSD(I,L) PROCESS DESIGN PARAMETER
              PRESSURE     TEMP   CAPACITY
  CDU               1        40        100
  ard             100        40        100
  vru               1        40        100
  tgt               1        40        100
  kd               10        40        100
  god              36        40        100
  hcr             140        40        100
  desal            10       120        100
  fcc               4        40        100     ;


* ACTUAL
TABLE PROCESSA(I,L) PROCESS ACTUAL  PARAMETER
              PRESSURE     TEMP   CAPACITY
  CDU               1        40        100
  ard             100        40        100
  vru               1        40        100
  tgt               1        40        100
  kd               10        40        100
  god              36        40        100
  hcr             140        40        100
  desal            10       120        100
  fcc               4        40        100     ;


PARAMETERS FWB Freshwater flowrate to boiler in T per hr;
           FWB = sum(i, ST(i))*1.03;
VARIABLES
COST          Total cost KD per year
FW(I)         Flowrate of freshwater to unit i in T per hr
REUSE(I,N)    Flowrate of water reuse from unit i to unit n in T per hr
CIN(I,M)      Inlet concentration of contaminant m to unit i in ppm
CROUT(M)      Outlet concentration of contaminant m from regeneration unit in ppm
FR(I)         Wastewater flow from unit i to regeneration unit in T per hr
FRU(I)        Regenerated water flow from regeneration unit to unit i in T per hr
FWTOT         Total freshwater demand in T per hr
REGENTOT      Total wastewater flowrate to regeneration unit in T per hr
WWFLOW        Total wastewater flowrate to water treatment and disposal in T per h
REUSETOT      Total wastewater reused in T per hr
DELTAMR(M)    Amount of contaminant m removed in regeneration unit in T per hr
FT(I)         Wastewater flowrate from unit i to treatment and disposal in T per h
```

```
FTR         Wastewater flowrate from regeneration unit to treatment and disposal
in T per hr;

POSITIVE VARIABLE FW, REUSE, CIN,  CROUT, FR, FRU, DELTAMR, FT, FTR,cmaxout1,
deltam;
POSITIVE VARIABLE FWTOT, REGENTOT, WWFLOW, REUSETOT;
****************************
* AVERAGE PROCESS TEMPERATURE    CONSIDERED
PROCESSA(I,"temp") =37;
* REGENERATOR IS LIMITED  TO EXISTING SIZE, REUSE IS FIXED AT 100 FOR BETTER
CONVERGENCE
REGENTOT.UP =165;
REUSETOT.UP=100;
**HYDRAULIC LIMITATION
ft.up('desal')=100;
ft.up('fcc')=20;
* REUSE FROM DESALTER IS PROHIBITED DUE TO SALT CONTENT
REUSE.UP('DESAL',I) = 0;
FW.LO('CDU')=0;
FW.LO('DESAL')=0;
fw.lo('ard')=0;
* REUSE FROM FCC IS PROHIBITED DUE TO CYANIDE CONTENT
FR.UP('FCC')=0;


PARAMETERS      cout(i,m) for correction ;
 cout('HCR','H2S') = cout1('HCR','H2S')*
                     (-.2407*(processa('hcr','temp')/processd('HCR','temp')*
processa('HCR','temp')/processd('HCR','temp'))
                     +.1197*(processa('HCR','temp')/processd('HCR','temp'))+1.1207)*
                     (-.4372*(processa('HCR','pressure')/processd('HCR','pressure')*
processa('HCR','pressure')/processd('HCR','pressure'))
                     +.905*(processa('HCR','pressure')/processd('HCR','pressure'))+(
5325);

 cout('HCR','NH3') = cout1('HCR','NH3')*
                     (-.1439*(processa('HCR','temp')/processd('HCR','temp')*
processa('HCR','temp')/processd('HCR','temp'))
                     +.1602*(processa('HCR','temp')/processd('HCR','temp'))+0.9827)*
                     (-.1023*(processa('HCR','pressure')/processd('HCR','pressure')*
processa('HCR','pressure')/processd('HCR','pressure'))
                     +.2116*(processa('HCR','pressure')/processd('HCR','pressure'))-
0.8907);


 cout('ARD','H2S')= cout1('ARD','H2S')*
                     (-.0402*(processa('ARD','temp')/processd('ARD','temp')*
processa('ARD','temp')/processd('ARD','temp'))
                     -.156*(processa('ARD','temp')/processd('ARD','temp'))+1.1949)*
                     (-.0323*(processa('ARD','pressure')/processd('ARD','pressure')
processa('ARD','pressure')/processd('ARD','pressure'))
                     +.2242*(processa('ARD','pressure')/processd('ARD','pressure'))
0.808);

 cout('ARD','NH3')= cout1('ARD','NH3')*
                     (-.0591*(processa('ARD','temp')/processd('ARD','temp')*
processa('ARD','temp')/processd('ARD','temp'))
```

```
                      +.0897*(processa('ARD','temp')/processd('ARD','temp'))+0.9686)*
                      (-.0402*(processa('ARD','pressure')/processd('ARD','pressure')*
processa('ARD','pressure')/processd('ARD','pressure'))

                      +.156*(processa('ARD','pressure')/processd('ARD','pressure'))+1
1949);

 cout('CDU','H2S')= cout1('CDU','H2S')*
                      (0.579*(processa('CDU','temp')/processd('CDU','temp')*processa(
CDU','temp')/processd('CDU','temp'))
                      -2.5345*(processa('CDU','temp')/processd('CDU','temp'))+2.9699)
*
                      (-.1265*(processa('CDU','pressure')/processd('CDU','pressure')*
processa('CDU','pressure')/processd('CDU','pressure'))
                      +1.217*(processa('CDU','pressure')/processd('CDU','pressure'))-
0.0919);

 cout('CDU','NH3')= cout1('CDU','NH3')*
                      (0.0712*(processa('CDU','temp')/processd('CDU','temp')*
processa('CDU','temp')/processd('CDU','temp'))
                      +.0854*(processa('CDU','temp')/processd('CDU','temp'))+1.051)*
                      (+.018*(processa('CDU','pressure')/processd('CDU','pressure')*
processa('CDU','pressure')/processd('CDU','pressure'))
                      +.0448*(processa('CDU','pressure')/processd('CDU','pressure'))+
1.0268);

 cout('VRU','H2S')= cout1('VRU','H2S')*
                      (-0.4341*(processa('VRU','temp')/processd('VRU','temp')*
processa('VRU','temp')/processd('VRU','temp'))
                      -.6339*(processa('VRU','temp')/processd('VRU','temp'))+2.0703)*
                      (-1.496*(processa('VRU','pressure')/processd('VRU','pressure')*
processa('VRU','pressure')/processd('VRU','pressure'))

+3.3138*(processa('VRU','pressure')/processd('VRU','pressure'))-0.8208);

 cout('VRU','NH3')= cout1('VRU','NH3');

 cout('TGT','H2S')= cout1('TGT','H2S')*
                      (-0.4735*(processa('TGT','temp')/processd('TGT','temp')*
processa('TGT','temp')/processd('TGT','temp'))
                      +0.6819*(processa('TGT','temp')/processd('TGT','temp'))+0.7838)
*
                      (-.0022*(processa('TGT','pressure')/processd('TGT','pressure')*
processa('TGT','pressure')/processd('TGT','pressure'))
                      +0.0399*(processa('TGT','pressure')/processd('TGT','pressure'))
0.9623);

 cout('TGT','NH3')= cout1('TGT','NH3')*
                      (-0.0815*(processa('TGT','temp')/processd('TGT','temp')*
processa('TGT','temp')/processd('TGT','temp'))
                      +1.1976*(processa('TGT','temp')/processd('TGT','temp'))+0.6087
*
                      (-.0015*(processa('TGT','pressure')/processd('TGT','pressure')
processa('TGT','pressure')/processd('TGT','pressure'))
                      +.0145*(processa('TGT','pressure')/processd('TGT','pressure'))
0.9871);
```

```
 cout('KD','H2S')= cout1('KD','H2S')*
                      (-0.0553*(processa('KD','temp')/processd('KD','temp')*processa(
KD','temp')/processd('KD','temp'))
                      -0.415*(processa('KD','temp')/processd('KD','temp'))+1.3567)*
                      (+.8418*(processa('KD','pressure')/processd('KD','pressure')*
processa('KD','pressure')/processd('KD','pressure'))
                      -1.9706*(processa('KD','pressure')/processd('KD','pressure'))+2
1536);

 cout('KD','NH3')= cout1('KD','NH3')*
                       (-0.1578*(processa('KD','temp')/processd('KD','temp')*processa
KD','temp')/processd('KD','temp'))
                      +0.2444*(processa('KD','temp')/processd('KD','temp'))+0.9117)*
                      (-.0046*(processa('KD','pressure')/processd('KD','pressure')*
processa('KD','pressure')/processd('KD','pressure'))
                      -.0101*(processa('KD','pressure')/processd('KD','pressure'))+1.
0055);

 cout('GOD','H2S')= cout1('GOD','H2S')*
                      (-0.0553*(processa('GOD','temp')/processd('GOD','temp')*
processa('GOD','temp')/processd('GOD','temp'))
                      -0.415*(processa('GOD','temp')/processd('GOD','temp'))+1.3567)*
                      (-.1536*(processa('GOD','pressure')/processd('GOD','pressure')*
processa('GOD','pressure')/processd('GOD','pressure'))
                      +0.7955*(processa('GOD','pressure')/processd('GOD','pressure'))
0.358);

 cout('GOD','NH3')= cout1('GOD','NH3')*
                       (-0.1578*(processa('GOD','temp')/processd('GOD','temp')*
processa('GOD','temp')/processd('GOD','temp'))
                      +0.2444*(processa('GOD','temp')/processd('GOD','temp'))+0.9117)
*
                      (0.0172*(processa('GOD','pressure')/processd('GOD','pressure')*
processa('GOD','pressure')/processd('GOD','pressure'))
                      +.051*(processa('GOD','pressure')/processd('GOD','pressure'))+1
0338);


 cout(i,'cl2') =cout1(i,'cl2');
 cout(i,'HCN') =cout1(i,'HCN');
 cout('desal',m)= cout1('desal',m);
 cout('fcc',m)= cout1('fcc',m);




EQUATIONS
         OBJFUN            Objective function
         REUSESAME(I)      Reuse from the same unit is not allowed
         CINLET(N,M)       Inlet concentration
         CINCONS(N,M)      Inlet concentration constraint
         COUTLET(N,M)      Outlet concentration
         COUTCONSAVERAGE   Outlet constraint FOR DESAL
         CROUTLET(M)       Outlet concentration of regeneration unit
         REGCON(M)         Regeneration unit concentration constraint
         MASSBAL(N)        Mass balance for a water using unit
         RMASSBAL          Mass balance for a regeneration unit
```

```
          FRESHWATER      Total freshwater demand
          REUSET          Total reused water between units
          SUMREG          Total regenerated water
          SUMWASTE        Total wastewater to treatment and disposal
          TOTFLOW1        Total water to unit 1
          TOTFLOW3        Total water to unit 3
          TOTFLOW4        Total water to unit 4
          TOTFLOW5        Total water to unit 5
          TOTFLOW6        Total water to unit 6
          TOTFLOW8        Total water to unit 8 ;




* COST FUNCTION
*** COST OF TREATMENT  FOR FCC TREATED WATER IS 0.20 AND TREATED WATER FROM REGEN
IS .09 AND DESALTER 0.11
OBJFUN  ..  COST =E= (FWCOST*FWTOT + RWCOST*REGENTOT + WTCOST*(WWFLOW-FT('DESAL')-
FTR-ft('fcc')) + RUCOST*REUSETOT+
              (.11)*FT('DESAL')+ (.09)*FTR+ft('fcc')*.2 )*24*365;

* NO REUSE DIRECTLY FROM THE SAME UNIT
REUSESAME(I) ..  REUSE(I,I) =E= 0;

* INLET IMPURITIES CONCENTRATION AND CONSTRAINT ON UNIT N
CINLET(N,M)  ..  CIN(N,M)*(FW(N)+sum(i, REUSE(i,N))+FRU(N)) =E= sum(i, REUSE(i,N)
COUT(i,M))+FRU(N)*CROUT(M);
CINCONS(N,M) ..  CIN(N,M) =L= CMAXIN(N,M);

* OUTLET IMPURITIES CONSTRAINT ON UNIT N
COUTLET(N,M) ..  (FW(N)+ST(N)+ sum(i, REUSE(i,N)) + FRU(N))*(COUT(N,M)-CIN(N,M))
E= 1000*DELTAM(N,M);

TOTFLOW1 ..  (FW('cdu')+ST('cdu')+ sum(i, REUSE(i,'cdu')) + FRU('cdu')) =G= TW('
cdu');
TOTFLOW3 ..  (FW('kd')+ST('kd')+ sum(i, REUSE(i,'kd')) + FRU('kd')) =G= TW('kd');
TOTFLOW4 ..  (FW('god')+ST('god')+ sum(i, REUSE(i,'god')) + FRU('god')) =G= TW('
god');
TOTFLOW5 ..  (FW('hcr')+ST('hcr')+ sum(i, REUSE(i,'hcr')) + FRU('hcr')) =G= TW('
hcr');
TOTFLOW6 ..  (FW('ard')+ST('ard')+ sum(i, REUSE(i,'ard')) + FRU('ard')) =G= TW('
ard');
TOTFLOW8 ..  (FW('fcc')+ST('fcc')+ sum(i, REUSE(i,'fcc')) + FRU('fcc')) =G= TW('
fcc');

***********************************
COUTCONSAVERAGE..  deltam('desal','cl2')*1000 =E= DSLIMIT;

* CONCENTRATION LIMIT OF REGENERATED WATER (ONLY ONE REGENERATOR IS ASSUMED)
CROUTLET(M)  ..  CROUT(M)*sum(i, FR(i)) =E= sum(i, FR(i)*COUT(i,M))-1000*DELTAMR
M);
REGCON(M)    ..  CROUT(M) =E= CRMINOUT(M);

* MATERIAL BALANCE FOR WATER USING UNIT
MASSBAL(N)   ..  FW(N)+ST(N)+ sum(i, REUSE(i,N)) - sum(i, REUSE(N,i)) + FRU(N) -
R(N) - FT(N) =E= 0;

```

```
* MATERIAL BALANCE FOR REGENERATION UNIT
RMASSBAL      ..  sum(i, FR(i)) - sum(i, FRU(i)) - FTR =E= 0;

* TOTAL FRESHWATER DEMAND
FRESHWATER    ..  FWTOT =E= sum(i, FW(i)) + FWB;

* TOTAL REUSED WATER
REUSET        ..  REUSETOT =E= sum(i, sum(n, REUSE(i,n)));

* TOTAL WATER FROM REGENERATION UNIT
SUMREG        ..  REGENTOT =E= sum(i, FR(i));

* TOTAL WASTEWATER TO TREATMENT AND DISPOSAL UNIT
SUMWASTE      ..  WWFLOW =E= sum(i, FT(i)) + FTR + 0.03*FWB/1.03;

MODEL SUPER / ALL/;
OPTION ITERLIM = 1000000;
*OPTION NLP = MINOS;
SOLVE SUPER USING NLP MINIMIZING COST;
DISPLAY COST.L, FW.L, REUSE.L, CIN.L,  CROUT.L, FR.L, FRU.L, FWTOT.L,
REGENTOT.L, WWFLOW.L, REUSETOT.L, DELTAMR.L, FT.L, FTR.L;

* Prepare Excel File
**********************************
execute "gams transdata xsave=s1"
FILE myfile / c:\REGENreuse.dat/;
put myfile;
myfile.pc=5;

 put 'Value of Cost Function (KD/year)';
 put COST.L//;
 put 'Total Freshwater Demand (T/hr)';
 put FWTOT.L:8:3/;

 put 'Boiler Feed Water (T/hr)';
 put FWB:8:3/;
 put 'Total Reuse Flowrate (T/hr)';
 put REUSETOT.L:8:3/;
 put 'Total Wastewater flow to regeneration unit (T/hr)';
 put REGENTOT.L:8:3/;
 put 'Total Wastewater flow to treatment & Disposal (T/hr)';
 put WWFLOW.L:8:3//;

 put 'Freshwater Flow to Units (T/hr)'/;
 put 'Unit';
 put 'Flow';
 loop (N, put/N.te(N); put FW.L(N):8:3);

 put //'Steam Flow to Units (T/hr)'/;
 put 'Unit';
 put 'Flow';
 loop (N, put/N.te(N); put ST(N):8:3);

 put //'Maximum inlet conc. to units (ppm)'/;
 put '  ';
 loop (M, put M.te(M));
 loop (N, put/N.te(N);
```

```
loop (M, put CMAXIN(N,M));

put //'Maximum outlet conc. from units (ppm)'/;
put '  ';
loop (M, put M.te(M));
loop (N, put/N.te(N);
loop (M, put cout(N,M)););

put //'Load of contaminants ino units @37 (ppm)' ;
put '  ';
loop (M, put M.te(M) '  ');
put /' ';
loop (M, put 'ppm' 'kg/hr');
loop (N, put/N.te(N);
loop (M, put cout(N,M):8:3; put cout(N,M):8:3););


put //'Reuse flowrates from one unit to another'/;
put '  ';
loop (N, put N.te(N));
loop (I, put/I.te(I);
loop (N, put REUSE.L(I,N):8:3););

put //'Inlet concentration of contaminant m to units'/;
put '  ';
loop (M, put M.te(M));
loop (I, put/I.te(I);
loop (M, put CIN.L(I,M):8:3););

put //'Outlet concentration of contaminant m from units'/;
put '  ';
loop (M, put M.te(M));
loop (I, put/I.te(I);
loop (M, put COUT(I,M):8:3););

put //'Outlet concentration of contaminant m from regenerator'/;
loop (M, put M.te(M));
put /;
loop (M, put CROUT.L(M):8:3);

put //'Wastewater flow to reg. from unit';
loop (I, put/I.te(I) put FR.L(I):8:3);

put //'Reg. water flow to unit';
loop (I, put/I.te(I) put FRU.L(I):8:3);

put //'Load removed from units'/;
put '  ';
loop (M, put M.te(M));
loop (I, put/I.te(I);
loop (M, put cout(I,M):8:3););

put //'Load removed from regenerator'/;
loop (M, put M.te(M));
put /;
loop (M, put DELTAMR.L(M):8:3);
```

```
put //'Wastewater flow from unit to treatment';
loop (I, put/I.te(I) put FT.L(I):8:3);

put //'Flow from reg to treatment';
put FTR.L:8:3/;
put //'temperature used in the program  ';
put PROCESSA('CDU','TEMP'):8:3/;

put //'Chloride  removed  ';
put DELTAM.L('DESAL','CL2'):8:3/;
```

```
---- VAR deltam

              LOWER     LEVEL     UPPER    MARGINAL

CDU  .H2S       .        0.511     +INF       .
CDU  .NH3       .       10.496     +INF       .
CDU  .CL2       .         .        +INF    9527.711
CDU  .HCN       .         .        +INF       .
ARD  .H2S       .     2866.942     +INF       .
ARD  .NH3       .     1867.616     +INF       .
ARD  .CL2       .         .        +INF       .
ARD  .HCN       .         .        +INF       .
VRU  .H2S       .        4.024     +INF       .
VRU  .NH3       .        3.174     +INF       .
VRU  .CL2       .        0.453     +INF       .
VRU  .HCN       .         .        +INF       .
TGT  .H2S       .       41.184     +INF       .
TGT  .NH3       .       31.357     +INF       .
TGT  .CL2       .        0.272     +INF       .
TGT  .HCN       .         .        +INF       .
KD   .H2S       .        1.307     +INF       .
KD   .NH3       .        0.444     +INF       .
KD   .CL2       .         .        +INF       .
KD   .HCN       .         .        +INF       .
GOD  .H2S       .       48.149     +INF       .
GOD  .NH3       .       11.682     +INF       .
GOD  .CL2       .         .        +INF       .
GOD  .HCN       .         .        +INF       .
HCR  .H2S       .      440.425     +INF       .
HCR  .NH3       .      213.749     +INF       .
HCR  .CL2       .         .        +INF       .
HCR  .HCN       .         .        +INF       .
DESAL.H2S       .         .        +INF   94603.748
DESAL.NH3       .        8.219     +INF       .
DESAL.CL2       .       26.484     +INF       .
DESAL.HCN       .        0.183     +INF       .
FCC  .H2S       .       54.119     +INF       .
FCC  .NH3       .        5.249     +INF       .
FCC  .CL2       .        0.543     +INF       .
FCC  .HCN       .        1.810     +INF       .


**** REPORT SUMMARY :        0     NONOPT
                             0 INFEASIBLE
                             0  UNBOUNDED
                             0     ERRORS
GAMS Rev 130  Windows NT/95/98                  07/02/05 15:22:53  PAGE      6
G e n e r a l   A l g e b r a i c   M o d e l i n g   S y s t e m
E x e c u t i o n


----     302 VARIABLE  COST.L                 =  1136202.497  Total cost KD per
                                                              year


----     302 VARIABLE  FW.L  Flowrate of freshwater to unit i in T per hr
```

```

                    ( ALL       0.000 )


----     302 VARIABLE  REUSE.L  Flowrate of water reuse from unit i to unit n in
                                T per hr

               CDU         ARD          KD         GOD         HCR

CDU                      4.379       0.427       1.111      10.706
VRU          0.889      30.325       2.273       6.967       4.896
KD                                               0.322       0.598


----     302 VARIABLE  CIN.L  Inlet concentration of contaminant m to unit i in
                              ppm

               H2S         NH3         CL2

CDU         80.000      63.344      10.000
ARD         50.000      52.577      10.000
KD          88.863     100.000      10.000
GOD        100.000     100.000      10.000
HCR        100.000     200.000      10.000
DESAL       10.000      10.000      10.000
FCC         10.000      10.000      10.000


----     302 VARIABLE  CROUT.L  Outlet concentration of contaminant m from
                                regeneration unit in ppm

H2S 10.000,    NH3 10.000,    CL2 10.000


----     302 VARIABLE  FR.L  Wastewater flow from unit i to regeneration unit in
                             T per hr

CDU 36.877,    ARD 68.900,    TGT 23.544,    KD   3.579,    GOD 14.900
HCR 17.200


----     302 VARIABLE  FRU.L  Regenerated water flow from regeneration unit to
                              unit i in T per hr

CDU    0.111,    ARD   33.695,    DESAL 91.224,    FCC   13.600


----     302 VARIABLE  FWTOT.L              =      143.633  Total freshwater
                                                            demand in T per hr
             VARIABLE  REGENTOT.L           =      165.000  Total wastewater
                                                            flowrate to
                                                            regeneration unit in
                                                            T per hr
             VARIABLE  WWFLOW.L             =      143.633  Total wastewater
                                                            flowrate to water
                                                            treatment and
                                                            disposal in T per hr
```

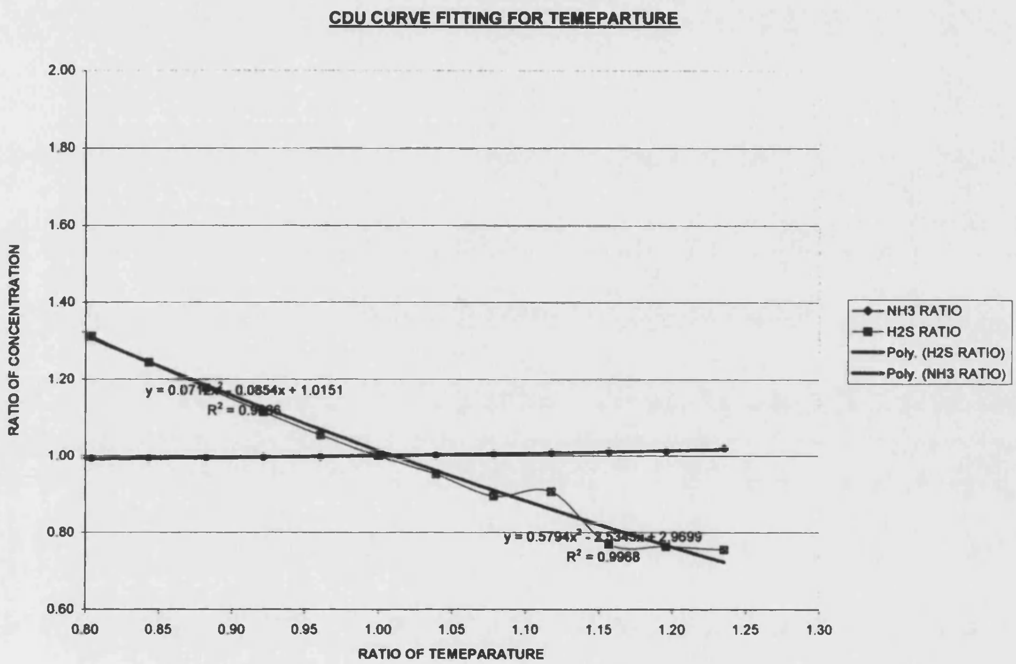
```
            VARIABLE  REUSETOT.L          =       62.894  Total wastewater
                                                          reused in T per hr


----     302 VARIABLE  DELTAMR.L  Amount of contaminant m removed in
                                  regeneration unit in T per hr

H2S 3400.830,    NH3 2137.373


----     302 VARIABLE  FT.L  Wastewater flowrate from unit i to treatment and
                             disposal in T per hr

TGT    3.656,    DESAL 91.324,    FCC   18.100


----     302 VARIABLE  FTR.L              =       26.370  Wastewater flowrate
                                                          from regeneration
                                                          unit to treatment
                                                          and disposal in T
                                                          per hr

**** REPORT FILE SUMMARY

myfile C:\REGENREUSE.DAT


EXECUTION TIME       =        0.265 SECONDS    1.6 Mb      WIN205-130


USER: Dr. Haitham Lababidi                           G020403:1117AP-WIN
      Kuwait University, Chemical Engineering Department        DC3752

**** FILE SUMMARY

INPUT      E:\SAR\PHD\GAMSFILES\CASE3 FOR REPORT.GMS
```

APPENDIX C

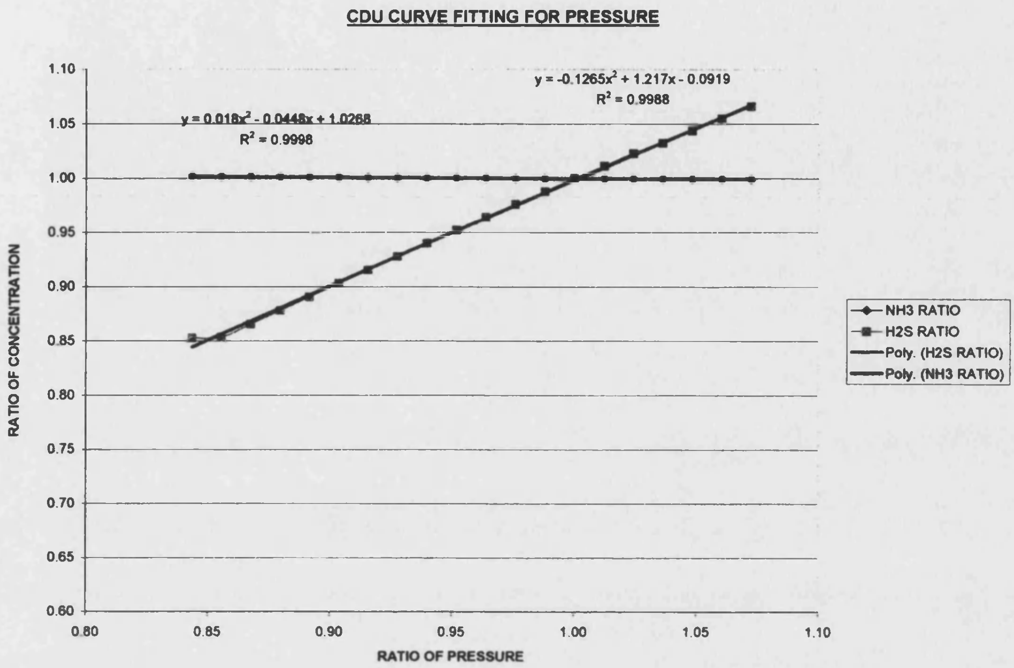
C. PLANT DATA AND SIMULATIONS

C.1. Crude unit operating data .

C.2. Curve fitting equation for temperature.



C.3. Curve fitting equation for Pressure



APPENDIX D
D. PUBLISHED PAPERS

D.1. Wastewater minimization under uncertain operational conditions

Suad A. Al-Redhwan[a], Barry D. Crittenden[b], Haitham M.S. Lababidi[c,*]
[a] *Process Engineering Division, Mina Al-Ahmadi Refinery, KNPC, P.O. Box 10252, Shuaiba 65453, Kuwait*
[b] *Department of Chemical Engineering, Faculty of Engineering and Design, University of Bath, Bath BA2 7AY, UK*
[c] *Chemical Engineering Department, College of Engineering and Petroleum, Kuwait University, P.O. Box 5969, Safat 13060, Kuwait*

Computer and Chemical Engineering.
Received 13 March 2004; received in revised form 18 September 2004; accepted 16 November 2004

D.2. Wastewater Optimization in Refineries Under Uncertainties in Mass Loads of Contaminants
54th Canadian Chemical Engineering Conference
Oct. 3-6 2004, Calgary, Alberta, Canada

Suad A. Al-Redhwan[a], Barry D. Crittenden[b], Haitham M.S. Lababidi[c,*]
[a] *Process Engineering Division, Mina Al-Ahmadi Refinery, KNPC, P.O. Box 10252, Shuaiba 65453, Kuwait*
[b] *Department of Chemical Engineering, Faculty of Engineering and Design, University of Bath, Bath BA2 7AY, UK*
[c] *Chemical Engineering Department, College of Engineering and Petroleum, Kuwait University, P.O. Box 5969, Safat 13060, Kuwait*

DTD 5
ARTICLE IN PRESS

ELSEVIER

Available online at www.sciencedirect.com
SCIENCE DIRECT®

Computers and Chemical Engineering xxx (2004) xxx–xxx

Computers & Chemical Engineering

www.elsevier.com/locate/compchemeng

Wastewater minimization under uncertain operational conditions

Suad A. Al-Redhwan[a], Barry D. Crittenden[b], Haitham M.S. Lababidi[c,*]

[a] *Process Engineering Division, Mina Al-Ahmadi Refinery, KNPC, P.O. Box 10252, Shuaiba 65453, Kuwait*
[b] *Department of Chemical Engineering, Faculty of Engineering and Design, University of Bath, Bath BA2 7AY, UK*
[c] *Chemical Engineering Department, College of Engineering and Petroleum, Kuwait University, P.O. Box 5969, Safat 13060, Kuwait*

Received 13 March 2004; received in revised form 18 September 2004; accepted 16 November 2004

Abstract

This paper addresses the problem of uncertainty in optimizing water networks in process industries. Due to the fact that wastewater flow rates as well as the levels of contaminants may vary widely as a result of changes in operational conditions and/or feedstock and product specifications, optimal wastewater network designs should be resilient and able to accommodate such changes.

Uncertainties considered in this study are derived from actual operational practice of major water-using units in a typical oil refinery of 400,000 barrels/day throughput. Rather than directly varying the concentrations and mass loads, only seasonal effects have been considered in this research to illustrate applications of the models.

Sensitivity analyses reveal that introducing uncertainty in operating conditions results in considerable changes in the connectivity of the units involved in wastewater reuse. The proposed stochastic optimization model produces a flexible wastewater network which is capable of accommodating uncertainties in operating temperature. In the presence of uncertainties, the optimal network minimizes the impact on the reuse connectivity (topology) by providing 32.2 t/h of freshwater in addition to the condensing steam. The stochastic approach adopted in this research has been found to be effective in handling uncertainties and has resulted in flexible and resilient wastewater networks with low expected value of perfect information (EVPI).

Keywords: Wastewater minimization; Uncertainty; Optimization; NLP; Stochastic programming

1. Introduction

The most serious challenges facing the chemical industries in the new millennium are their impacts on the environment. The enormous amount of industrial waste coupled with the growing awareness of the consequences of discharging effluents to natural resources has spurred the process industries to become more environmentally conscious and adopt a more proactive role. Over the past two decades, significant efforts have been made to reduce the quantity of industrial wastes generated. In recent years the focus has shifted from downstream pollution control (end-of-pipe treatment) to a more proactive practice of trying to prevent pollution at the source of its generation.

One major pollution-generating stream produced by almost all process industries is wastewater. Water is vital in a number of processes. It may be used as a heat sink and a heat source as well as a medium for extracting impurities from process streams. Hence, it is important to consider wastewater minimization as part of any pollution prevention activity.

Water is becoming an increasingly scarce commodity, especially in the Gulf Co-Operation Council (GCC) countries, and it is now becoming a potentially limiting factor for agricultural and even for industrial developments. Wastewater minimization should be given the highest priority in efforts to seek non-conventional sources of water that can be utilized to supplement ground water and desalinated water. Wastewater minimization has a great potential to play in water resource management and can be used to lessen the imbalance in demand versus supply.

* Corresponding author. Tel.: +965 4811188; fax: +965 4839498.
E-mail address: lababidi@kuc01.kuniv.edu.kw (H.M.S. Lababidi).

0098-1354/$ – see front matter © 2004 Published by Elsevier Ltd.
doi:10.1016/j.compchemeng.2004.11.002

Nomenclature

C_{FW}	unit cost of freshwater (KD/t)
C_{RU}	unit cost of direct wastewater reuse (KD/t)
C_{RW}	unit cost of wastewater regeneration-reuse (KD/t)
C_{WT}	unit cost of wastewater treatment and disposal (KD/t)
$C^{\mathrm{in}}_{m,i}$, $C^{\mathrm{out}}_{m,i}$	concentration of contaminant m in the inlet and outlet streams of unit/regenerator i, respectively (ppm)
$C^{\mathrm{in,max}}_{m,i}$, $C^{\mathrm{out,max}}_{m,i}$	maximum allowable concentration of contaminant m at the inlet and outlet of unit/regenerator i, respectively (ppm)
$C^{\mathrm{out,min}}_{m,r}$	minimum concentration of contaminant m in the outlet stream of regeneration unit r (ppm)
$F_{i,j}$	flow rate of direct wastewater reuse from unit i to unit j (t/h)
$\mathrm{FG}_{j,r}$	flow rate of wastewater from regeneration unit j to another regeneration unit r (t/h)
$\mathrm{FR}_{i,r}$, $\mathrm{FR}_{r,i}$	flow rate of wastewater from water-using unit i to regeneration unit r, or from regeneration unit r to water-using unit i, respectively (t/h)
FTR_r	flow rate of wastewater from regenerator r to wastewater treatment and disposal plant (t/h)
FTU_i	flow rate of wastewater from unit i to wastewater treatment and disposal plant (t/h)
FW_i	flow rate of freshwater to water-using unit i (t/h)
KD	Kuwaiti Dinar, 1 KD = US$ 3.3
M	set of contaminants
N	set of water-using units
R	set of regeneration units
s	scenario index
S_i	flow rate of steam used in unit i (t/h)
$\Delta w_{m,i}$	mass load of contaminant m transferred from unit i to water stream (kg/h)

Greek letters

ω	outcomes of random experiments
Ω	set of all outcomes of random experiments

Methods available for wastewater minimization are basically integration techniques (El-Halwagi, 1997). These techniques can include hierarchical analysis (Crittenden, 2001; Douglas, 1992; Rossiter, Spriggs, & Klee, 1993), pinch analysis (Linhoff & Smith, 1994; Prakotpol & Srinophakun, 2004; Tainsh & Rudman, 1999), mass-exchange networks (El-Halwagi, 1997; Hallale & Frase, 2000) and mathematical programming (Bagajewicz, 2000; Cohen & Allen, 1992; El-Halwagi & Spriggs, 1995; Mann & Liu, 1999; Papalexandri, Pistikopoules, & Floudas, 1994). Each method varies significantly in scope and approach.

Mathematical optimization is the most suitable approach for wastewater minimization, for both new and retrofit applications. A number of optimization models have been proposed (Bagajewicz, Rodera, & Savelski, 2000; Doyle & Smith, 1997; El-Halwagi, 1995; Huang, Chang, Ling, & Chang, 1999; Roberge, Sikora, & Baetz, 1994; Rossiter & Nath, 1995; Savelski & Bagajewicz, 2003). Alva-Argáez, Vallianatos, and Kokossis (1999) presented conceptual formulations that combine insights from Pinch technology with mathematical programming. They introduced a mixed integer linear transhipment formulation that enables easy screening and scoping ahead of the network development. Bagajewicz (2000) presented a review of the mathematical programming procedures for designing and retrofitting water networks, with an emphasis on refinery processes. They concluded that mathematical programming can efficiently produce globally optimal and sub-optimal solutions if conceptual insights are made to properly build the models. The author commented also that practical numerical challenges are still apparent.

Most of the mathematical models available in literature have attempted the water reuse problem by assuming that water always removes fixed loads of contaminants. Another assumption is that solubility and corrosion limits can be used to set maximum inlet and outlet concentration units imposed on contaminants. These assumptions are necessary to simplify the problem and making it easier to solve (Bagajewicz, 2000). Doyle and Smith (1997) considered the two cases in targeting maximum water reuse. The optimization problems were formulated as a nonlinear problem for the fixed mass load assumption, and a linear problem for the fixed outlet concentration assumption. The authors combined the proposed mathematical method with graphical representation which incorporates various types of constraints.

For many systems, concentrations of contaminants may reach their solubility limits, but such limits are functions of process parameters (temperature and pressure). Hence the loads of contaminants are variable with respect to the flow rate (Huang et al., 1999). This suggests that the design of wastewater networks should be resilient and able to accommodate different pollutant levels (Bagajewicz, 2000) which may easily result from deviations in operating conditions.

The impact of uncertainties on optimal wastewater networks has not been studied, except by Linniger, Chakraborty, and Colberg (2000). They studied waste reduction in a batch process for pharmaceutical production using an uncertainty model, which was incorporated essentially to facilitate decision making for the solvent recovery and treatment process. However, there is a rich literature in studying the effect of uncertain parameters on the resiliency of heat exchanger networks (Aguilera & Nasini, 1995; Floudas & Ciric, 1989; Galli & Cerda, 1991; Hu, Chen, & Shen, 1993). Recently, a number of researchers have reinitiated the area of "process design under uncertainty". Cheng, Subrahmanian, and Westerberg (2003) provided a brief review of this area and formulated design and planning under uncertainty as a multi-objective decision process.

In this paper we address the problem of uncertainty in optimizing wastewater networks in the process industries. Due to the fact that wastewater flow rates and levels of contaminants can vary widely as a result of changes in operational conditions and/or feedstock and product specifications, optimal water network designs should be resilient and able to accommodate such changes. Accordingly, a stochastic programming approach is proposed to accommodate uncertainty in designing or retrofitting industrial wastewater networks.

A three-step methodology has been developed in the current research. First, a deterministic optimization model was developed and tested. This model searches for the network configuration with minimum freshwater use and optimal wastewater reuse and regeneration/reuse. In this paper, the term "reuse" is used in the case of a water stream which can be used directly without any treatment whilst the term "regeneration/reuse" is used when it is necessary for a wastewater stream to be treated before it can be used again. The second step involves a sensitivity analysis in which uncertainty is introduced as maximum and minimum ranges in operating conditions. In the third step, a stochastic formulation is developed based on the two-stage recourse problem method with finite number of realization (Birge & Louveaux, 1997; Cheng et al., 2003).

The proposed three-step methodology has been tested on a typical oil refinery wastewater network. The proposed methodology is however quite generic and, accordingly, can be applied to any process industry. Refinery operations have been selected because they possess several major chemical units in which water is used intensively. Examples include steam stripping, liquid–liquid extraction and washing operations. Uncertainties have been derived from actual operational practices with the major refinery water-using units. Rather than directly varying the concentrations and mass loads, seasonal effects have been used in this study to illustrate the application of the proposed methodology.

2. Deterministic optimization model

General schematic diagrams of water-using and regeneration units are shown in Fig. 1. A water-using unit receives freshwater in addition to recycled water streams from other units and regenerators. In addition, certain units utilize steam for direct contact with material for stripping and heating purposes. Condensed steam is considered as a wastewater source because it contains contaminants transferred from the feedstock of the processing unit. Effluents from this unit are directed to three possible destinations: to other units as direct reuse, to the regeneration units for partial removal of selected contaminants, or to wastewater treatment and disposal. A regeneration unit (Fig. 1) receives wastewater streams from the water-using units as well as from other regeneration units for further removal of contaminants. Effluents from the regeneration units are recycled back to the water-using units, sent to other regeneration operations, or to the wastewater treatment and disposal plant.

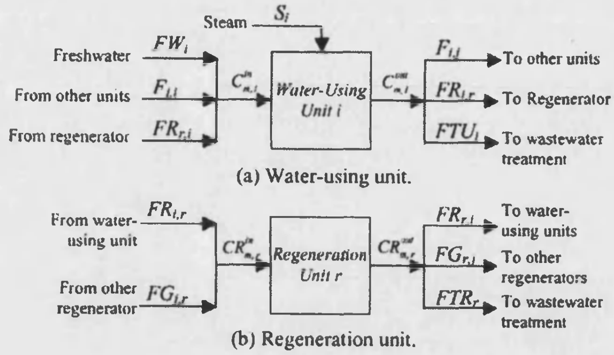


Fig. 1. Input/output structure of general water-using and regeneration units.

The optimization model is based on minimizing the total cost of the wastewater network. The cost items include: freshwater cost, water recycle/reuse cost, partial wastewater regeneration cost, and wastewater treatment and disposal cost. For a set of N water-using units and R regeneration units, the objective function may be defined as:

$$\text{Min}\left\{ C_{\text{FW}}\sum_{i=1}^{N}\text{FW}_i + C_{\text{RU}}\sum_{i=1}^{N}\sum_{\substack{j=1\\ j\neq i}}^{N} F_{i,j} + C_{\text{RW}}\sum_{r=1}^{R}\sum_{i=1}^{N}\text{FR}_{r,i} + C_{\text{WT}}\left(\sum_{i=1}^{N}\text{FTU}_i + \sum_{r=1}^{R}\text{FTR}_r\right)\right\} \quad (1)$$

where C_{FW}, C_{RU}, C_{RW}, and C_{WT} are unit costs (KD/t) of freshwater, wastewater reuse, regeneration-reuse, and wastewater treatment and disposal, respectively. These costs are assumed constant for all units. The regeneration/treatment costs are assumed also the same for all contaminants and treatment units. FW_i is the freshwater demanded by unit i, $F_{i,j}$ the water reuse flow rate from unit i to unit j, and $\text{FR}_{r,i}$ the regenerated water flow rate from regenerator r to unit i. FTU_i and FTR_r are wastewater flow rates from unit i and regeneration unit r, respectively.

The objective function expressed by Eq. (1) is subject to the following constraints:

(a) For a set of M contaminants, the inlet concentration of contaminant, m, should not exceed the maximum allowable concentration, $C_{m,i}^{\text{in,max}}$:

$$C_{m,i}^{\text{in}} \leq C_{m,i}^{\text{in,max}} \quad (2)$$

The average inlet concentration of contaminant m, $C^{\text{in}}_{m,i}$ can be expressed as:

$$C^{\text{in}}_{m,i} = \frac{\sum\limits_{\substack{j=1\\ j\neq i}}^{N} F_{j,i}C^{\text{out}}_{m,j} + \sum\limits_{r=1}^{R} \text{FR}_{r,i}C^{\text{out}}_{m,r}}{\text{FW}_i + \sum\limits_{\substack{j=1\\ j\neq i}}^{N} F_{j,i} + \sum\limits_{r=1}^{R} \text{FR}_{r,i}}, \quad \forall i \in N, \forall m \in M \qquad (3)$$

Substituting the value of $C^{\text{in}}_{m,i}$ and rearranging, constraint (2) becomes:

$$\text{FW}_i C^{\text{in,max}}_{m,i} + \sum_{\substack{j=1\\ j\neq i}}^{N} F_{j,i}[C^{\text{in,max}}_{m,i} - C^{\text{out}}_{m,j}] + \sum_{r=1}^{R} \text{FR}_{r,i}[C^{\text{in,max}}_{m,i} - C^{\text{out}}_{m,r}] \geq 0, \quad \forall i \in N, \forall m \in M \qquad (4)$$

$C^{\text{out}}_{m,j}$ and $C^{\text{out}}_{m,r}$ are the concentrations of contaminant m in outlet streams from unit j and regenerator r, respectively.

(b) To maximize water reuse, the outlet concentration of contaminants from a water-using unit is forced to be equal to a limiting outlet concentration. This limiting outlet concentration may be specified based on a number of considerations, such as solubility limits, operating conditions, in addition to regeneration and process design limits. Hence, the maximum outlet concentration of contaminants will be forced to be equal to a pre-specified limit, $C^{\text{out,max}}_{m,i}$:

$$C^{\text{out}}_{m,i} = C^{\text{out,max}}_{m,i} \qquad (5)$$

The difference between the input and output concentrations of the contaminants, entering and leaving a water-using unit, is proportional to the mass load of contaminant that is transferred from the waste stream to the water stream. Hence, for a set of M contaminants, a component balance for contaminant, m, for the water-using unit, i, can be expressed as:

$$C^{\text{out}}_{m,i} = C^{\text{in}}_{m,i} + \frac{\Delta w_{m,i} \times 10^3}{\text{FW}_i + S_i + \sum\limits_{\substack{j=1\\ j\neq i}}^{N} F_{j,i} + \sum\limits_{r=1}^{R} \text{FR}_{r,i}}, \quad \forall i \in N, \forall m \in M \qquad (6)$$

$\Delta w_{m,i}$ is the mass load of contaminant, m, transferred from unit i to the water stream. Note that concentrations are expressed in ppm, mass loads of contaminants in kg/h, and flow rates in t/h.

Substituting the values of $C^{\text{in}}_{m,i}$ and $C^{\text{out}}_{m,j}$ from Eqs. (3) and (6), respectively, and rearranging, the outlet concentration constraint (5) becomes:

$$\left(\text{FW}_i + S_i + \sum_{\substack{j=1\\ j\neq i}}^{N} F_{j,i} + \sum_{r=1}^{R} \text{FR}_{r,i}\right) \times (C^{\text{in}}_{m,i} - C^{\text{out,max}}_{m,i}) = \Delta w_{m,i} \times 10^3, \quad \forall i \in N, \forall m \in M \qquad (7)$$

(c) A regeneration unit is required to reduce the concentration of specific contaminant(s) to a pre-specified minimum limit, $C^{\text{out,min}}_{m,r}$:

$$C^{\text{out}}_{m,r} = C^{\text{out,min}}_{m,r} \qquad (8)$$

For a regeneration unit r, the outlet concentration of contaminant m is equal to the inlet concentration less the amount removed.

$$C^{\text{out}}_{m,r} = C^{\text{in}}_{m,r} - \frac{\Delta w_{m,r} \times 10^3}{\sum\limits_{i=1}^{N} \text{FR}_{i,r} + \sum\limits_{\substack{j=1\\ j\neq r}}^{R} \text{FG}_{j,r}}, \quad \forall r \in R, \forall m \in M \qquad (9)$$

$\Delta w_{m,r}$ represents the mass load of contaminant m removed by the regenerator r. Moreover, the concentration of contaminants at the inlet of the regenerator can be expressed as:

$$C^{\text{in}}_{m,r} = \frac{\sum\limits_{i=1}^{N} \text{FR}_{i,r}C^{\text{out}}_{m,i} + \sum\limits_{\substack{j=1\\ j\neq r}}^{R} \text{FG}_{j,r}C^{\text{out}}_{m,r}}{\sum\limits_{i=1}^{N} \text{FR}_{i,r} + \sum\limits_{\substack{j=1\\ j\neq r}}^{R} \text{FG}_{j,r}}, \quad \forall r \in R, \forall m \in M \qquad (10)$$

Substituting Eqs. (9) and (10) and rearranging, constraint (8) becomes:

$$\sum_{i=1}^{N} \text{FR}_{i,r}(C^{\text{out,min}}_{m,r} - C^{\text{out}}_{m,i}) + \sum_{\substack{j=1\\ j\neq r}}^{R} \text{FG}_{j,r} \times (C^{\text{out,min}}_{m,r} - C^{\text{out}}_{m,j}) = -\Delta w_{m,r} \times 10^3, \quad \forall r \in R, \forall m \in M \qquad (11)$$

$FG_{j,r}$ is the wastewater flow rate from regenerator j to another regenerator r.

(d) Material balances for water-using units:

$$FW_i + S_i + \sum_{\substack{j=1 \\ j \neq i}}^{N} (F_{j,i} - F_{i,j}) + \sum_{r=1}^{R} (FR_{r,i} - FR_{i,r}) - FTU_i = 0, \quad \forall i \in N \qquad (12)$$

(e) Material balances for regeneration units:

$$\sum_{i=1}^{N} (FR_{i,r} - FR_{r,i}) + \sum_{\substack{j=1 \\ j \neq r}}^{R} (FG_{j,r} - FG_{r,j}) - FTR_r = 0, \quad \forall r \in R \qquad (13)$$

(f) All concentrations and flow rates are positive:

$$FW_i,\ S_i,\ F_{i,j},\ FR_{i,r},\ FG_{r,q},\ FTU_i,\ FTR_r \geq 0,$$
$$C^{\mathrm{in}}_{m,i},\ C^{\mathrm{out}}_{m,i},\ C^{\mathrm{out}}_{m,r} \geq 0, \quad \forall i, j \in N, \forall r, q \in R, \forall m \in M \qquad (14)$$

3. Stochastic programming

The stochastic programming technique adopted in this study is the two-stage stochastic linear program with fixed recourse, which is also known as the scenario analysis technique (Birge & Louveaux, 1997). The underlying idea is to simultaneously consider multiple scenarios of an uncertain future, each with an associated probability of occurrence. The model simultaneously determines an optimal contingency plan for each scenario and an optimal plan that optimally hedges against these contingency plans. Optimization entails maximization or minimization of expected net profits or expected costs, where expected refers to multiplying net profits or costs associated with each scenario by its probability of occurrence.

In this technique, uncertainty is represented in terms of random variables resulting from a number of random experiments with outcomes denoted by ω, where the set of all outcomes is represented by Ω. In studying the wastewater minimization problem, the random outcomes range from throughput and operating conditions to feedstock and product specifications. The random variables of interest may be the freshwater demand, amounts of reuse and regeneration-reuse, or the size of the regeneration and treatment units. The relevant set of outcomes is clearly problem-dependent. Also, it is usually not essential to be able to define these outcomes accurately because the focus is mainly on their impact on the random variables. The particular values of the various random variables are only known after the random experiment. Decisions are then divided into two groups:

- A number of decisions have to be taken before the experiment. All these decisions are called *first-stage decisions* and the period when these decisions are taken is called the *first stage*.
- A number of decisions can be taken after the experiment. They are called *second-stage decisions*. The corresponding period is called the *second stage*.

The two-stage stochastic program with fixed recourse may be defined as:

$$\min z = c^{\mathrm{T}} x + E_{\omega}[\min q(\omega)^{\mathrm{T}} y(\omega)],$$
$$\text{s.t. } Ax = b, \quad T(\omega)x + Wy(\omega) = h(\omega), \quad x \geq 0 \text{ and } y(\omega) \geq 0 \qquad (15)$$

First-stage decisions are represented by the vector x, while second-stage decisions are represented by the vector $y(\omega)$ or $y(\omega, x)$, which are functions of the outcome of the random experiment and of the first-stage decisions. The objective function contains a deterministic term, $c^{\mathrm{T}}x$, and the expectation of the second-stage objective, $q(\omega)^{\mathrm{T}}y(\omega)$, taken over all realizations of the random event ω. For a given realization of the random events, $\omega \in \Omega$, the second-stage problem data $q(\omega)$, $h(\omega)$ and $T(\omega)$ become known, and then the second-stage decisions, $y(\omega, x)$, must be taken. E_{ω} is the probability of occurrence of the random outcome ω.

4. Stochastic optimization model

For the wastewater minimization problem considered in this study, two types of problems may be identified. The first one involves designing the network, while the second problem involves decisions on the inventories (flow rates) for fixed freshwater resources. These problems will be termed as "Stochastic Design" and "Stochastic Operational" problems. For the former, direct wastewater reuse may be considered as the first-stage decision variable, whilst freshwater demands and regeneration-reuse amounts are the second-stage variables. Stochastic operational solutions are needed for cases when resources are limited, as well as for planning purposes. For these instances, it would be useful to determine the optimal freshwater demands that will minimize the cost of the wastewater network in the presence of uncertainties. In this case, freshwater demands will be considered as the first-stage decision variables, whilst reuse and regeneration-reuse amounts are the second-stage decision variables.

Stochastic design problems are more effective in developing resilient wastewater networks, and at the same time applicable for both grassroots' design and retrofit problems. Nonetheless, operational stochastic problems may be applied on existing wastewater networks to study variations in freshwater demands and capacities of regeneration and treatment plants.

For the wastewater minimization problem presented in the current study, the stochastic optimization model will be derived for the stochastic design problem. In this model, uncertainty is introduced through the assumption that the random variables emerge from three scenarios, namely, "*low*", "*normal*", or "*high*". The "*low*" and "*high*" scenarios, for instance, may be assumed to be a 5% decrease or increase in the nominal (design level) load of contaminants, respectively. It is useful here to index these decisions by a scenario index $s = 1$, 2, 3 corresponding to "low", "normal", or "high" conditions, respectively.

First-stage decisions are considered to be the amounts of wastewater reuse, $F_{i,j}$, whilst freshwater demand, FW_i, regeneration-reuse, $\mathrm{FR}_{r,i}$, and the amounts sent to the wastewater treatment and disposal plant, FTU_i and FTR_r, are considered as second-stage decisions. This creates a new set of variables of the form FW_i^s, FTU_i^s and FTR_r^s. For instance, FW_4^3 represents the volume of freshwater demanded by unit '4', when the level of contaminants, for instance, is higher than the normal level.

The probability of occurrence is defined for each scenario by the set $E_\omega = \{\omega_1, \omega_2, \omega_3\}$, where $\omega_1 + \omega_2 + \omega_3 = 1$. Consequently, the objective function of the stochastic model may be derived from the deterministic objective function (Eq. (1)) and represented as follows:

$$\mathrm{Min}\left\{ C_{\mathrm{FW}} \sum_{s=1}^{3} \sum_{i=1}^{N} \omega_s \mathrm{FW}_i^s + C_{\mathrm{RU}} \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} F_{i,j} + C_{\mathrm{RW}} \sum_{s=1}^{3} \sum_{r=1}^{R} \sum_{i=1}^{N} \omega_s \mathrm{FR}_{r,i}^s + C_{\mathrm{WT}} \sum_{s=1}^{3} \omega_s \times \left(\sum_{i=1}^{N} \mathrm{FTU}_i^s + \sum_{r=1}^{R} \mathrm{FTR}_r^s \right) \right\} \quad (16)$$

This stochastic objective function minimizes the cost of the wastewater network while accounting for the possibility of occurrence of the s scenarios. However, it would result in only one decision concerning the direct reuse variable, $F_{i,j}$.

Similarly, constraints (4), (7), and (11)–(14) should be modified and represented in terms of the first- and second-decision variables. The maximum allowable concentration constraints (Eqs. (4)) may be defined for the three scenarios ($s = 1$–3) as:

$$\mathrm{FW}_i^s C_{m,i}^{\mathrm{in,max}} + \sum_{\substack{j=1 \\ j \neq i}}^{N} F_{j,i}[C_{m,i}^{\mathrm{in,max}} - C_{m,j}^{\mathrm{out},s}] + \sum_{r=1}^{R} \mathrm{FR}_{r,i}^s [C_{m,i}^{\mathrm{in,max}} - C_{m,r}^{\mathrm{out},s}] \geq 0, \quad \forall i \in N, \forall m \in M, s = 1, 2, 3 \quad (17)$$

Operational uncertainties directly affect the mass load of contaminants, $\Delta w_{m,i}$, transferred from the units to the water streams. Hence, the stochastic model would result in different mass loads for different scenarios. Accordingly, $\Delta w_{m,i}^s$ is introduced and constraint (7) is expressed in terms of the three scenarios as:

$$\left(\mathrm{FW}_i^s + S_i + \sum_{\substack{j=1 \\ j \neq i}}^{N} F_{j,i} + \sum_{r=1}^{R} \mathrm{FR}_{r,i}^s \right) (C_{m,i}^{\mathrm{in},s} - C_{m,i}^{\mathrm{out,max}}) = \Delta w_{m,i}^s \times 10^3, \quad \forall i \in N, \forall m \in M, s = 1, 2, 3 \quad (18)$$

Note that, in the current implementation, the steam amounts, S_i, are assumed to be constant to satisfy the stripping requirements of the processes. The stochastic version of constraints (11)–(14) may be similarly represented as:

$$\sum_{i=1}^{N} \mathrm{FR}_{i,r}^s (C_{m,r}^{\mathrm{out,min}} - C_{m,i}^{\mathrm{out},s}) + \sum_{\substack{j=1 \\ j \neq r}}^{R} \mathrm{FG}_{j,r}^s (C_{m,r}^{\mathrm{out,min}} - C_{m,j}^{\mathrm{out},s}) = -\Delta w_{m,r}^s \times 10^3, \quad \forall r \in R, \forall m \in M, s = 1, 2, 3 \quad (19)$$

$$\mathrm{FW}_i^s + S_i + \sum_{\substack{j=1 \\ j \neq i}}^{N} (F_{j,i} - F_{i,j}) + \sum_{r=1}^{R} (\mathrm{FR}_{r,i}^s - \mathrm{FR}_{i,r}^s) - \mathrm{FTU}_i^s = 0, \quad \forall i \in N, s = 1, 2, 3 \quad (20)$$

$$\sum_{i=1}^{N} (\mathrm{FR}_{i,r}^s - \mathrm{FR}_{r,i}^s) + \sum_{\substack{j=1 \\ j \neq r}}^{R} (\mathrm{FG}_{j,r}^s - \mathrm{FG}_{r,j}^s) - \mathrm{FTR}_r^s = 0, \quad \forall r \in R, s = 1, 2, 3 \quad (21)$$

$$\mathrm{FW}_i^s, S_i, F_{i,j}^s, \mathrm{FR}_{i,r}^s, \mathrm{FG}_{r,q}^s, \mathrm{FTU}_i^s, \mathrm{FTR}_r^s \geq 0,$$
$$C_{m,i}^{\mathrm{in},s}, C_{m,i}^{\mathrm{out},s}, C_{m,r}^{\mathrm{out},s} \geq 0, \quad \forall i, j \in N, \forall r, q \in R, \forall m \in M, s = 1, 2, 3 \quad (22)$$

Both the deterministic and stochastic optimization models are NLP formulations which have been solved using the CONOPT2 solver within GAMS (Brooke, Kendrick, Meeraus, & Raman, 1998). The deterministic formulation, for the case study discussed in the next section, entails 147 constraints, 203 continuous variables, 1416 non-zero elements 940 of which are nonlinear, and an execution time of 0.12

Table 1
Nominal water demands and maximum allowable inlet and design outlet concentrations for the base case (Case-0)

Unit	Demand (t/h)		Maximum allowable inlet concentration and design outlet concentration (ppm)								Wastewater
	Water	Steam	H_2S		NH_3		Cl_2		HCN		
Boiler	143.6		0	0	0	0	0	0	0	0	4.15
CDU	1.0	52.50	80	89	80	259	10	10	0	0	53.50
VDU		45.35	50	99	50	70	10	10	0	0	45.35
TGT		27.20	80	1514	200	1152	10	10	0	0	27.20
HCR	16.2	1.00	100	25700	200	12627	10	10	0	0	17.20
GOD	8.4	6.50	100	3331	100	884	10	10	0	0	14.90
ARD	68.4	0.50	50	41660	200	27158	10	10	0	0	68.90
KD	2.7	1.80	100	379	100	198	10	10	0	0	4.50
FCC	13.6	4.50	10	3000	100	300	10	40	0	100	18.10
DES	88.6	0.10	20	10	50	100	20	300	0	0	88.7
Total	342.1	139.45									342.1

CPU seconds in a 2.9 GHz Pentium 4 processor. A typical stochastic case study involves 426 constraints, 445 continuous variables, 4105 non-zero elements (2838 nonlinear), and 0.18 CPU seconds.

5. Refinery wastewater network—base case

The case studies discussed below are related to a wastewater network of a typical 400,000 barrel per stream day oil refinery. This network consists of nine water and steam using units, which include an atmospheric crude distillation unit (CDU), a vacuum distillation/rerun unit (VDU), a tail gas treatment unit (TGT), a hydrocracking unit (HCR), a gas oil desulfurization unit (GOD), an atmospheric residue desulfurization unit (ARD), a kerosene desulfurization unit (KD), a fluid catalytic cracking unit (FCC), and a desalting unit (DES).

Four contaminants are considered: ammonia, chlorine, hydrogen cyanide and hydrogen sulfide. NH_3 and H_2S exist in all units and streams, while the sources of Cl_2 and HCN are from the DES and FCC units, respectively. Nominal water and steam demands of each unit, in addition to the concentration limits and contaminant concentrations, are listed in Table 1. These values have been derived from actual design and licensor data.

The cost function proposed above (Eq. (1)) is based on minimizing the total cost of the wastewater network. The cost factors used to estimate the freshwater cost and the cost of water reuse, regeneration and wastewater treatment and disposal are listed in Table 2.

Table 2
Cost of freshwater, reuse, regeneration and treatment

Type of water	Cost in KD[a]/t
Freshwater, C_{FW}	0.60
Regenerated water, C_{RW}	0.10
Reuse water, C_{RU}	0.05
Wastewater treatment and disposal, C_{WT}	1.00

[a] 1 KD = US$ 3.3.

The case presented in Table 1 will be referred to as the base case (Case-0) against which results of other case studies will be compared. For this case, wastewater streams are neither reused nor regenerated-reused. The total freshwater demand amounts to 342.1 t/h, of which 143.6 t/h is supplied to the boiler for steam generation. The wastewater network for Case-0 is shown in Fig. 2.

The next case study (Case-1) considers water reuse, in which the wastewater generated by one unit is reused in other units, without any regeneration or treatment. Using the deterministic optimization model, the freshwater demand for Case-1 was found to be 264 t/h, that is, a 23% reduction in the amount of wastewater compared to the base case (Case-0). The optimization results for this case are summarized in Table 3.

The results for Case-1 show that reusable wastewater comes from the fractionation units, namely the CDU and VDU. These two units are major steam consuming units in the refinery. About 80% of the wastewater generated by condensing steam in the CDU is reused in other units and about 60% of the VDU wastewater is reused. On the other hand, wastewater from conversion units such as the HCR and ARD cannot be reused without regeneration due to the high concentrations of H_2S, and NH_3.

Case-2 considers the situation where wastewater is reused in other units after suitable partial treatment. The capacity of the regenerator is limited to 165 t/h. Freshwater demand for this case is 179 t/h (i.e. a 47% reduction compared to Case-0). Optimum wastewater flow rates to and from the regeneration unit are listed in Table 4. In addition to the amounts used for steam generation, freshwater is only demanded by the desalter (DES), while other units utilize regenerated wastewater.

In a further case study both reuse and regeneration-reuse options were allowed. In other words, wastewater generated in one unit is reused in other units either directly or after regeneration. By allowing both options, maximum benefit can be achieved. This case will be referred to as Case-3, and will act as a reference for the rest of the case studies that will be developed later to demonstrate the effect of uncertainty on

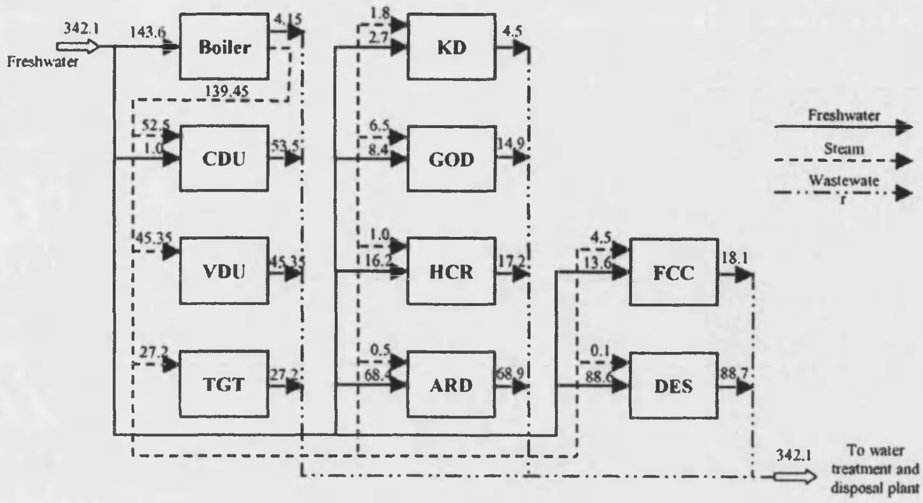


Fig. 2. Wastewater network for the base case (Case-0).

Table 3
Optimization results for wastewater reuse, Case-1

From unit	Reuse: to units (t/h)									
	CDU	ARD	VDU	TGT	KD	GOD	HCR	DES	FCC	To all
Boiler	–	–	–	–	–	–	–	–	–	–
CDU	–	8				1	11	10	2	32
ARD		–								
VDU	1	30	–		2	7	5			45
TGT				–						
KD					–		1			1
Total	1	38			2	8	17	10	2	78

Table 4
Optimization results for wastewater regeneration-reuse, Case-2

	Steam (t/h)	Freshwater (t/h)	Wastewater (t/h)		
			To regeneration unit	To treatment unit	From regeneration unit
Boiler	–	143.6		4.18	–
CDU	52.5			53.5	1.0
ARD	0.5		68.9		68.4
VDU	45.35		36.8	8.55	
TGT	27.2		27.2		
KD	1.8			4.5	2.7
GOD	6.5		14.9		8.4
HCR	1.0		17.2		16.2
DES	0.1	35.3		90.1	54.7
FCC	4.5			18.1	13.6
Regeneration unit	–		–		–
Total	139.45	178.9	165	178.9	165

the wastewater network. The optimum wastewater network for Case-3 is shown schematically in Fig. 3. The resultant network demands only 143.6 t/h, that is a 58% reduction in wastewater compared to the base case, Case-0. This means that freshwater is consumed by the boiler only for steam generation. All other units utilize condensed steam in addition to reused and/or regenerated-reused streams.

6. Operational uncertainties

The main source of uncertainty that will be considered in this paper is variations in operating conditions. A direct consequence of variations in operating conditions is changes in the amounts (loads) of contaminants in different process units. Hence, variations arise in the concentrations and flow

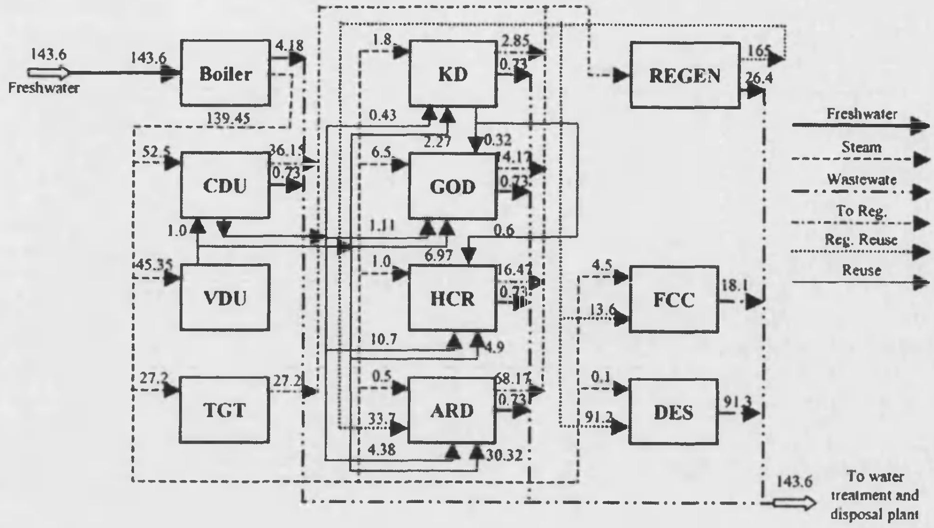


Fig. 3. Wastewater network for reuse and regeneration-reuse (Case-3).

rates of wastewater streams. Factors contributing to uncertainties in operating conditions include variations in operating temperatures and pressures, throughputs and yields, operating modes, and the quality of both the feedstock and product slates. For illustrative purposes in the current study, sources of operational uncertainties will be limited to variations in operating temperatures and pressures only.

The operating temperatures of the fractionation columns are usually manipulated to meet product requirements, as well as to compensate for seasonal changes in the ambient temperature. Fluctuations in the cooling water supply temperature to the overhead exchanger have a direct effect on the overhead receiver temperature where sour water is in equilibrium with the process fluid. Actual experience in operating such processes indicates that the concentration of contaminants decreases at higher operating temperatures and vice versa. This
is due to the fact that the contaminants (H_2S and NH_3) be- 492
come more volatile at higher temperature and tend to escape 493
with the vapour split, leaving a lower load of contaminants 494
to be washed by water. At the same time, the solubility of 495
contaminants in water increases at higher temperature. Such 496
a dual effect is thereby an interesting source of uncertainty. 497

Effects of variations in ambient temperature and oper- 498
ating pressure on the concentrations (loads) of the con- 499
taminants for each water-using unit have been monitored 500
for 1 year. This involved analyzing water samples, which 501
were collected daily, to determine the concentrations of var- 502
ious contaminants. Sample data for the overhead cooler 503
of the crude distillation unit (CDU) is shown in Fig. 4. 504
This plot demonstrates clearly that H_2S concentration in- 505
creases at low cooling seawater temperatures and vice 506
versa.

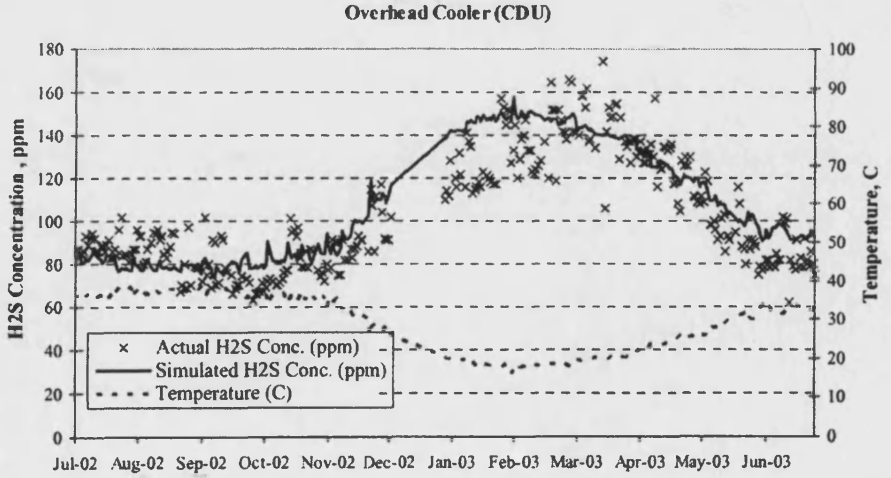


Fig. 4. Variations of H_2S content in the wastewater from the overhead of the CDU unit with seawater cooling temperature. Comparing actual and simulated concentrations.

Table 5
Contaminant loads (kg/h) at different operating temperatures

Unit	Low: 35 °C		Normal: 37 °C		High: 39 °C	
	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3
CDU	5.1	20.6	4.8	20.8	4.5	21.0
VDU	4.3	3.2	4.0	3.2	3.8	3.2
TGT	41.5	30.4	41.2	31.4	40.7	32.3
HCR	448.9	218.3	442.2	217.2	434.8	216.0
GOD	51.0	13.2	49.6	13.2	48.2	13.1
ARD	2902.8	1872.7	2870.4	1871.3	2837.3	1869.3
KD	1.8	0.9	1.7	0.9	1.7	0.9
FCC	54.6	5.5	54.6	5.5	54.6	5.5
DES	0.9	9.1	0.9	9.1	0.9	9.1

Collected plant data was found not sufficient for quantifying and modelling the effect of uncertainty in operating conditions on the concentrations of the contaminants. To be more representative and efficient, the prediction model should cover a wider range of variations and consider combinations of various sources of uncertainty. For this reason, a process simulator (SIMSCI, PRO II) was used to estimate the quantities of sour water produced and the concentration of contaminants for various operating conditions. Simulation results were compared with the actual concentration measurements (see Fig. 4) and found reasonably close. Finally, a number of correlations were obtained, from the simulation results, for estimating the load of the contaminants as a function of operating temperature and pressure.

As a result, each water-using unit has been associated with a set of correlation capable of predicting the concentration of the contaminants, for different intervals of operating conditions. Computational difficulties were avoided by formulating the correlations as linear functions of temperature and pressure. For certain instances, linearity was achieved by dividing the operating horizon into fine intervals and deriving the correlation for each interval. The correlations were then incorporated in the optimization model and represented as GAMS expressions. Table 5 shows sample results of deviations in the loads of various contaminants for a temperature change of only 2 °C below and 2 °C above the nominal operating temperature, which is 37 °C. The case studies (Case-0 to Case-3) presented above are for the 37 °C operating temperature. It is clear that deviations are not the same for all units. This provides an excellent indication that the uncertainties considered in this study are not artificial, but are rather extracted from actual operation of the units. Note that the loads listed in Table 5 are for uncertainty in the temperature of the overhead of the fractionation column only.

7. Sensitivity analysis results

Four sensitivity analysis cases have been conducted to study the effect of uncertainties in operational conditions on the optimal wastewater network. The first two cases (Case-4 and Case-5) assume that the operating temperature varies from 32 °C in winter to 42 °C in summer, respectively, keeping operating pressure fixed at nominal (design) values. The other two cases (Case-6 and Case-7) assume ±5% deviations in operating pressure from the nominal (design) conditions, while the operating temperature is fixed at 37 °C. Optimal wastewater networks for these cases have been determined using the deterministic model together with the developed correlations. The optimization results are summarized and compared in Table 6 against the reference case, Case-3, which involves both wastewater reuse and regeneration-reuse.

The optimization results of various wastewater networks will be compared using two criteria. The first is the freshwater demand, whilst the second is the amount of wastewater reuse and regeneration-reuse. The latter provides an indication as to whether a modification of topology (i.e. changes to connections between different units) is required. Accordingly, a network design which is resilient to variations in operating conditions is the network that is capable of accommodating changes in freshwater demands, and with a flexible topology to account for variations in wastewater reuse and regeneration-reuse.

The sensitivity analysis results, listed in Table 6, reveal that all four scenarios (Case-4 to Case-7) demand the minimum freshwater amount, 143.6 t/h. Hence, freshwater is only used for steam generation. However, the results related to wastewater reuse from the fractionation units, CDU and VDU, indicate that topology modifications might be necessary. For a 5 °C decrease or 5 °C increase in operating temperature, the amounts of direct reuse from the CDU to different units decreased by 35% and increased by 11.8%, respectively. Con-

Table 6
Sensitivity analysis results

Case	Condition	Freshwater (t/h)	Reuse from[a]		Cost (MMKD[b]/year)
			CDU	VDU	
Case-3	Ref. 37 °C	143.6	16.62	45.46	1.136
Case-4	32 °C	143.6	11.25	45.35	1.245
Case-5	42 °C	143.6	18.95	45.35	1.108
Case-6	−5% pressure	143.6	48.01	17.57	1.123
Case-7	+5% pressure	143.6	16.19	45.35	1.141
Case-8	Stochastic ±5 °C	143.6–175.8	16.37	45.35	1.199

[a] 1 KD = US$ 3.3.
[b] Reuse from KD to GOD and HCR is also needed for Case-5 and Case-7.

versely, reuse amounts from the VDU unit are not affected. Reuses from both units vary widely with variations in operating pressure. An increase in pressure at the CDU has a higher impact on contaminant concentrations compared to the VDU for the same variation in pressure. However the cost is slightly affected.

It is obvious from the sensitivity analysis results that the topology of the optimal wastewater network would vary significantly as a result of uncertainty in operating temperature and pressure. The results of the reference case, Case-3 (Fig. 3), show that wastewater from the CDU and VRU units are reused in various units. If the wastewater network is designed based on these results, then slight deviations in operating conditions would result in a network incapable of handling the demanded flow rates, or connections (piping and pumping) with minimum utilization.

8. Stochastic optimization results

It is evident from the sensitivity analysis results that the optimal wastewater network is affected significantly by only slight variations in operating temperature and pressure. Due to the fact that nominal conditions vary widely to meet yield and throughput requirements, and perfect operational information is not always available, it is useful to determine a wastewater network that is both economical and at the same time flexible to operate. We will now demonstrate how stochastic programming may be used to determine such a network.

The approach used is the two-stage stochastic linear programming with fixed recourse, introduced above. For the stochastic case, uncertainty is assumed only in operating temperature. The stochastic programming model is solved for ±5 °C deviations in the ambient (cooling water) temperature as an example. Accordingly, three scenarios will be considered: *low*, *average*, and *high*, corresponding to operating at 32, 37 and 42 °C, respectively. It is also assumed that the probabilities of occurrence of these three scenarios (ω_1, ω_2, and ω_3) are 25%, 50% and 25%, respectively. This means that low and high temperatures are expected for 3 months each, whilst normal operating conditions are for 6 months.

For the stochastic design problem, it is required to determine the optimal network design (topology or connectivity) that will lessen the effect of uncertainty in operating temperature on the minimum cost of the network. Ac-

Table 7
Optimization results for the stochastic problem, Case-8

Units	Reuse from		Scenarios	Freshwater	Wastewater		
	CDU	VDU			From regeneration unit	To regeneration unit	To treatment unit
Boiler				143.6			4.18
CDU	–	0.89	Low		0.11	32.3	4.83
			Average		0.11	32.3	4.83
			High		0.29	29.86	7.44
ARD	3.91	29.62	Low		34.87	68.9	
			Average		34.87	68.9	
			High	32.2	4.01	70.25	
VDU		–	Low				
			Average				
			High				
TGT			Low			27.2	
			Average			27.2	
			High			27.2	
KD	0.41	2.29	Low			4.5	
			Average			4.5	
			High			4.6	
GOD	1.289	7.11	Low			14.9	
			Average			14.9	
			High			15.17	
HCR	10.76	5.44	Low			17.2	
			Average			17.2	
			High			17.94	
DES			Low		91.23		91.33
			Average		91.23		91.33
			High		91.23		91.33
FCC			Low		13.6		18.1
			Average		13.6		18.1
			High		13.6		18.1
Total	16.37	45.35	Low	143.6	139.81	165	114.26
			Average	143.6	139.81	165	114.26
			High	175.8	109.13	165	116.87

cordingly, the first-stage decision variables are the amounts of direct reuse between the process units, and so the freshwater demands will be considered as second-stage decision variables.

The stochastic optimization results for this case are represented by Case-8 in Table 7. This case study resulted in the determination of the optimum topology (connectivity) between the units that would accommodate the consequences of variations in operating temperature. Direct wastewater reuse is from the two fractionation units (CDU and VDU). Additionally, the stochastic program determined the optimum values of the second-stage variables for each of the three assumed scenarios. The minimum freshwater demand is 143.6 t/h (utilized for steam generation), whilst the maximum freshwater demand is 175.8 t/h. The maximum freshwater demand will be necessary in case the worst scenario (lowest operating temperature) were to occur. This means that 32.2 t/h of freshwater should be readily available to be used, in addition to the condensing steam (143.6 t/h). In practice, such information is quite useful for planning utility utilization. The optimal stochastic solution can be understood as follows: at the nominal operating condition, condensing steam would be sufficient to satisfactorily remove the contaminants. Variations in the operating conditions will however result in disturbance to the reuse and regeneration-reuse amounts, which will need to be compensated by the additional freshwater utilization not exceeding 32.2 t/h.

This solution serves to demonstrate that it is impossible, under conditions of uncertainty, to find a solution that is ideal under all circumstances. Condensing steam needs to be supported by a surplus freshwater amount that may or may not need to be used. Such decisions can appear in a stochastic model because decisions have to be balanced or hedged against various scenarios.

The hedging effect has an important impact on the expected optimal cost. The optimal cost of the stochastic case, Case-8, is KD 1,198,880 per year, which lies between the costs of the temperature sensitivity analysis cases, Case-4 and Case-5 (see Table 6). Assuming that perfect information is available about variations in operating conditions, one would provide a different operational procedure for each scenario. The annual cost of the combined scenarios would be then evaluated as the weighted mean of the three costs, namely KD 1,156,565 (possibility of occurrence is 25% for 32 °C, 50% for 37 °C and 25% for 42 °C). This is the cost realized under perfect information.

Since we have no prior information on the occurrence of uncertainties, the best option is to design the network based on the stochastic solution, Case-8. This results in a network with optimal cost of KD 1,198,880 per year. The difference between this cost and the perfect information cost, namely KD 42,315 per year is called the *expected value of perfect information* (EVPI). This additional cost is due to the presence of uncertainty. The EVPI within this particular refinery example is only 3.5% of the optimal cost of the network, and is exceptionally low.

9. Conclusions and further research

Wastewater minimization in the presence of uncertainties involves the optimal design of wastewater networks which are resilient to variations in operational conditions. A three-step methodology has been developed to achieve this. First, a deterministic optimization model has been developed and tested. It searches for the network configuration with minimum freshwater use and optimal wastewater reuse or regeneration-reuse. The second step involves a sensitivity analysis in which uncertainty has been introduced as maximum and minimum ranges in operating conditions. Finally, a stochastic formulation has been developed, based on the scenario-analysis stochastic programming approach.

The optimization models are NLP problems which are effectively solved using GAMS. They have been tested on a typical refinery wastewater network. The proposed methodology can nonetheless be applied to any process industry. Refinery operations have been selected in the current research because they include many of the major unit operations in which water is intensively utilized. Unit operations include steam stripping, liquid–liquid extraction and washing operations. Four contaminants have been included in this study: H_2S, NH_3, Cl_2 and HCN. In addition, uncertainties considered in this study have been derived from actual operational practices with major water-using units in the typical oil refinery.

The results of the deterministic model indicate that a 58% reduction in freshwater (from 342 to 143.6 t/h) can be achieved by incorporating reuse and regeneration-reuse options. The deterministic network design uses freshwater only for steam generation. Condensing steam was found to be sufficient for all water-using units.

The sensitivity analysis considered the effect of 5 °C variations in operating temperature above and below the nominal conditions, and ±5% deviations in operating pressures. The sensitivity analyses reveal that uncertainties in operating conditions have a direct and significant effect on the connectivity (topology) of the wastewater network. Even though relatively minor deviations in operating temperature and pressure have been assumed, the optimal networks would nonetheless need major modifications to their connectivity.

The proposed stochastic programming approach resulted in a resilient wastewater network capable of accommodating uncertainty in operating conditions. The network compensates disturbances in the reuse and regeneration-reuse amounts by utilizing a surplus freshwater amount. At normal operating conditions, freshwater is only used for steam generation and all water-using units are serviced using condensed wastewater. On the other hand, at the utmost deviation in operating temperature, the network demands 32.2 t/h of freshwater, keeping the connectivity the same. Furthermore, the optimal design resulting from the stochastic model has a very low additional cost due to uncertainty (EVPI) which amounts to only 3.5% of the total cost.

Work is currently in progress to incorporate other sources of uncertainty which may include variations in throughput, type or quality of feedstock (crude oil) and operating modes. In addition, research is continuing on accounting for multiple sources of uncertainties. The current implementation of the stochastic optimization model accounts only for a single source of uncertainty. This was demonstrated above for deviations in operating temperatures, and can be easily applied for uncertainty in operating pressure. But the challenging research task is to integrate, for instance, both temperature and pressure effects simultaneously. Such a task is not straightforward due to the fact that the effects of such operational uncertainties are not directly related to the mass loads of the contaminants, $\Delta w_{m,i}$. In other words, deviations are not introduced directly to decision variables, but rather are determined from a number of correlations which are represented as constraints in the optimization formulation. One potential solution is to add more scenarios to describe different combinations of the uncertainty sources (e.g. "low temperature and nominal pressure").

References

Aguilera, N., & Nasini, G. (1995). Flexibility test for heat exchanger networks with uncertain flowrates. *Computers and Chemical Engineering, 19*(9), 1007–1017.

Alva-Argáez, A., Vallianatos, A., & Kokossis, A. (1999). A multi-contaminant transhipment model for mass exchange networks and wastewater minimisation problems. *Computers and Chemical Engineering, 23*, 1439–1453.

Bagajewicz, M. (2000). A review of recent design procedures for water networks in refineries and process plants. *Computer and Chemical Engineering, 24*, 2093–2113.

Bagajewicz, M., Rodera, H., & Savelski, M. (2000). A robust method to obtain optimal and sub-optimal design and retrofit solutions of water utilization systems with multiple contaminants in process plants. In *Proceedings of the Seventh International Symposium on Process Systems Engineering (PSE)*.

Birge, J. R., & Louveaux, F. (1997). *Introduction to stochastic programming. Springer series in operations research*. New York: Springer-Verlag.

Brooke, A., Kendrick, D., Meeraus, A., & Raman, R. (1998). *GAMS—a user's guide*. N.W., Washington, DC, USA: GAMS Development Corporation, http://www.gams.com.

Cheng, L., Subrahmanian, E., & Westerberg, A. W. (2003). Design and planning under uncertainty: Issues on problem formulation and solution. *Computers and Chemical Engineering, 27*, 781–801.

Cohen, Y., & Allen, D. (1992). An integrated approach to process waste minimization research. *Journal of Hazardous Materials, 29*, 237–253.

Crittenden, B. D. (2001). *Clean technology 1, sections 2 and 3*. Bath: University of Bath.

Douglas, J. M. (1992). Process synthesis for waste minimization. *Industrial and Engineering Chemistry Research, 31*, 238–243.

Doyle, S. J., & Smith, R. (1997). Targeting water reuse with multiple contaminants. *Transactions of International Chemical Engineering, Part B, 73*(3), 181–189.

El-Halwagi, M. M. (1995). Introduction to numerical optimization approach to pollution prevention. In A. P. Rossiter (Ed.), *Waste minimization through process design* (pp. 199–208). New York: McGraw-Hill.

El-Halwagi, M. M. (1997). *Pollution prevention through process integration—systematic design tools*. California, USA: Academic Press.

El-Halwagi, M. M., & Spriggs, H. D. (1995). Solve the design puzzles with mass integration. *Chemical Engineering Progress*, 25–44.

Floudas, C. A., & Ciric, A. R. (1989). Strategies for overcoming uncertainties in heat exchanger network synthesis. *Computers and Chemical Engineering, 13*(10), 1133–1152.

Galli, M. R., & Cerda, J. (1991). Synthesis of flexible heat exchanger networks: III. Temperature and flowrate variations. *Computers and Chemical Engineering, 15*(1), 7–24.

Hallale, N., & Fraser, D. M. (2000). Super targeting for mass exchange networks. *Transactions of the Institution of Chemical Engineers, Part A, 78*, 202–216.

Hu, S., Chen, B., & Shen, J. (1993). Nonconvex feasible region of heat exchanger networks with uncertain stream parameters. *Chinese Journal of Chemical Engineering, 1*(2), 74–83.

Huang, C. H., Chang, C. T., Ling, H. C., & Chang, C. C. (1999). A mathematical model for water usage and treatment network design. *Industrial and Engineering Chemistry Research, 38*, 2666–2679.

Linhoff, B., & Smith, R. (1994). Recent development in pinch analysis. In *Paper Presented at Process System Engineering*.

Linniger, A. A., Chakraborty, A., & Colberg, R. D. (2000). Planning of waste reduction strategies under uncertainty. *Computers and Chemical Engineering, 24*, 1043–1048.

Mann, J. G., & Liu, Y. A. (1999). *Industrial water reuse and wastewater minimization*. NY: McGraw-Hill Professional Engineering (Chapter 9), p. 10011.

Papalexandri, K. P., Pistikopoules, E. N., Floudas, C. A. (1994). Synthesis of mass exchanger networks for the waste minimization: An MINLP approach. In *Proceedings of the IChemE Symposium Series no. 133* (pp. 351–358).

Prakotpol, D., & Srinophakun, T. (2004). GAPinch: Genetic algorithm toolbox for water pinch technology. *Chemical Engineering and Processing, 43*(2).

Roberge, H. D., Sikora, R. P., & Baetz, B. W. (1994). Use of optimization modelling to evaluate industrial waste reduction options: Application to a sour gas plant. *Waste Management, 14*(7), 649–654.

Rossiter, A. P., & Nath, R. (1995). Wastewater minimization using non-linear programming. In A. Rossiter (Ed.), *Waste minimization through process design*. McGraw-Hill Publications (Chapter 17).

Rossiter, A. P., Spriggs, D., & Klee, H., Jr. (1993). Apply process integration to waste minimization. *Chemical Engineering Progress*.

Savelski, M., & Bagajewicz, M. (2003). On the necessary conditions of optimality of water utilizations systems in process plants with multiple contaminants. *Chemical Engineering Science, 58*, 5349–5362.

Tainsh, R. A., & Rudman, A. R. (1999). Practical techniques and methods to develop an efficient water management strategy. In *Paper Presented at IQPC Conference on Water Recycling and Efficient Re-Use*.

Kuwait University
College of Graduate School
Chemical Engineering Department

Wastewater Optimization in Refineries Under Uncertainties in Mass Loads of Contaminants

Suad A. Al-Redhwan
Barry D. Crittenden
Haitham M.S. Lababidi

54th Canadian Chemical Engineering Conference
Oct. 3-6 2004, Calgary, Alberta, Canada

October 2004

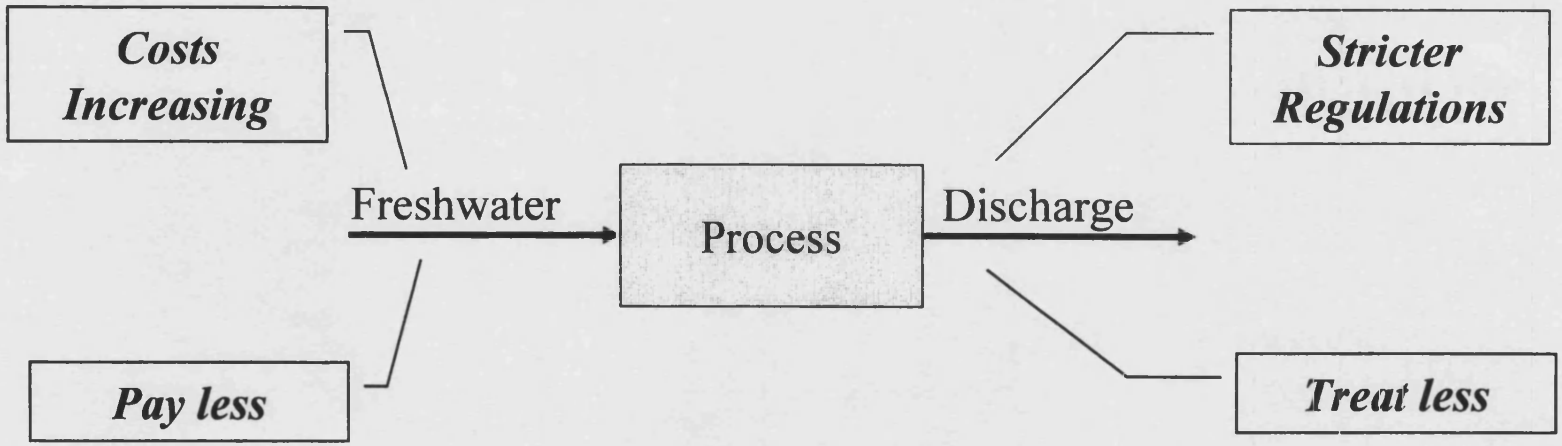
Objective

Study the impact of operational uncertainties on optimal refinery wastewater networks

- Aim
  - Design wastewater networks that are resilient to variations in operating conditions

Introduction

- Wastewater Minimization
  - *Pollution prevention / End-of-pipe treatment*



Introduction

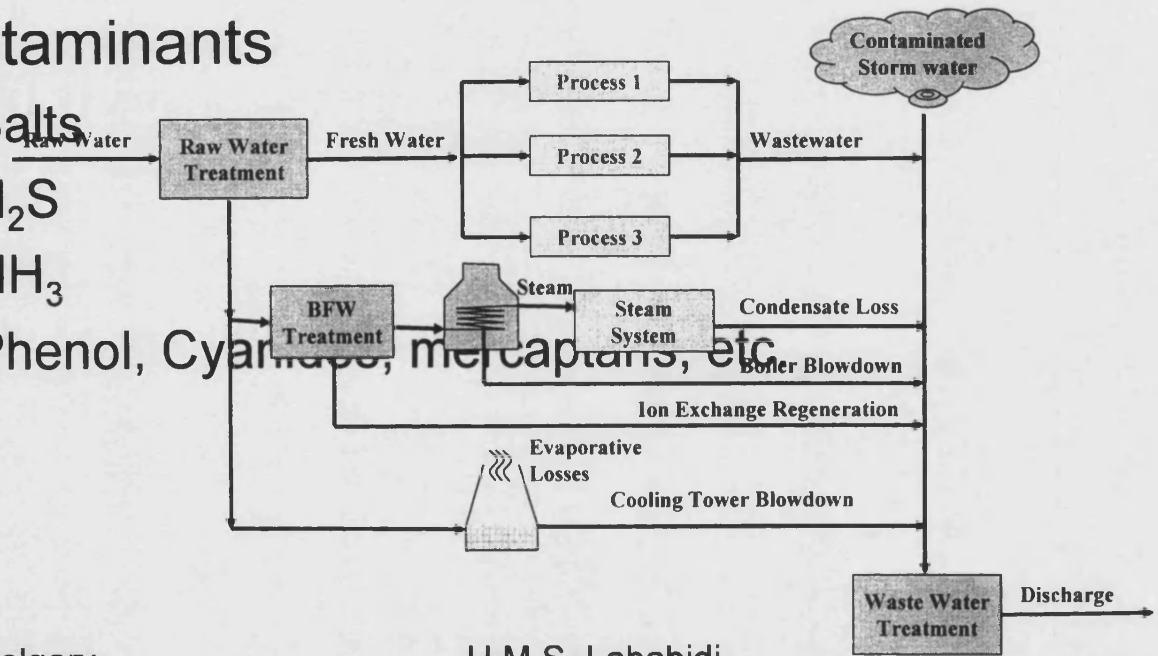
- Wastewater Minimization
  - Process integration techniques
    - Hierarchical analysis
    - Pinch analysis
    - Mass exchange networks
    - Mathematical Programming
      - Real problems
      - Root design and retrofit
      - Multiple contaminants

Introduction

- Reducing effluent volume and load
  - Reuse
  - Regenerate and Reuse
  - Regenerate/Reuse

Introduction

- Wastewater minimization in refineries
  - Water is used extensively
    - ➢ Steam-using operations
    - ➢ Water-using operations
  - Contaminants
    - ➢ Salts
    - ➢ H_2S
    - ➢ NH_3
    - ➢ Phenol, Cyanides, mercaptans, etc.



Introduction

- Common assumptions
  - Fixed mass load
    - ➢ Water removes fixed amount of contaminants
  - Fixed maximum inlet and outlet concentrations
    - ➢ Based on solubility, corrosion limits, etc.

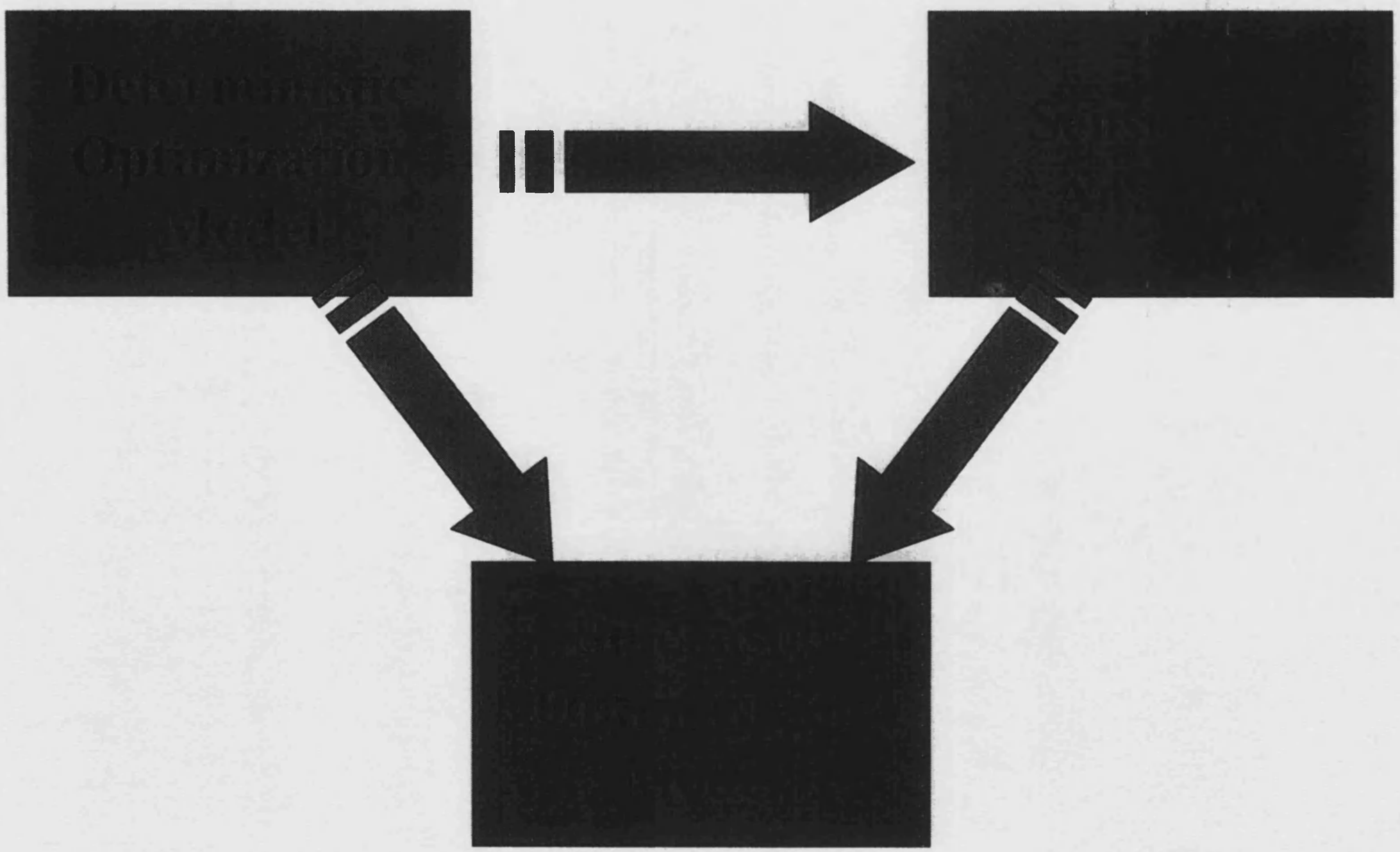
- BUT
  - Mass loads and concentration limits are function of operating conditions.
  - What is the impact of such uncertainty

Uncertainty

Unit	Low: 35°C		Normal: 37°C		High: 39°C	
	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3
CDU	5.1	20.6	4.8	20.8	4.5	21.0
VDU	4.3	3.2	4.0	3.2	3.8	3.2
TGT	41.5	30.4	41.2	31.4	40.7	32.3
HCR	448.9	218.3	442.2	217.2	434.8	216.0
GOD	51.0	13.2	49.6	13.2	48.2	13.1
ARD	2902.8	1872.7	2870.4	1871.3	2837.3	1869.3
KD	1.8	0.9	1.7	0.9	1.7	0.9
FCC	54.6	5.5	54.6	5.5	54.6	5.5
DES	0.9	9.1	0.9	9.1	0.9	9.1

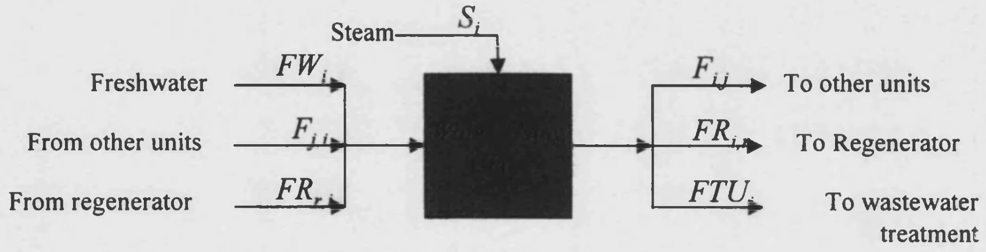
Contaminant loads (kg/hr) at different cooling water temperatures

Methodology

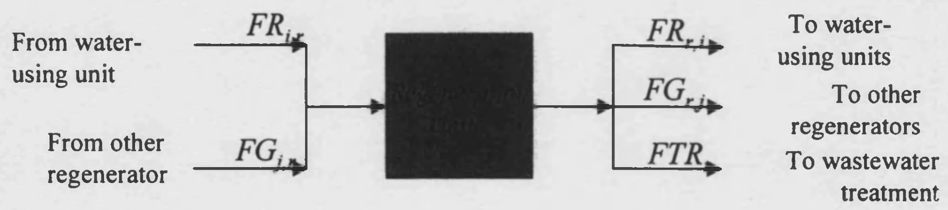


Deterministic Model

- Water-Using Units



- Steam-Using Units



Objective Function

Minimizing the total cost of the wastewater network.

Cost items include: freshwater cost, water recycle/reuse cost, partial wastewater regeneration cost, and wastewater treatment and disposal cost

Constraints

- ✓ Material balance for water-using unit
- ✓ Material balance for regeneration unit
- ✓ Maximum allowable concentration
- ✓ Maximum water reuse
- ✓ Regenerator duty

Stochastic Approach

- Two-stage stochastic programming with fixed recourse
  - Also known as *scenario analysis* technique
- Multiple scenarios of an uncertain future
  - associated probability of occurrence
- Determines an optimal contingency plan for each scenario
  - First-stage decisions
  - Second-stage decisions

Stochastic Approach

- Stochastic Design Problem
  - First-stage Decision:
    - Direct wastewater reuse (Topology)
  - Second-stage Decisions:
    - Freshwater demands
    - Regeneration/reuse amounts
- Stochastic Operation Problem
  - First-stage Decision:
    - Freshwater demands
  - Second-stage decisions
    - Direct wastewater reuse
    - Regeneration/reuse amounts

Stochastic Approach

- Uncertainty in mass load of contaminants
  - ± 5% deviations from base-case
  - Three scenarios:
    - ➢ "mass load is *low*" → 95% Base → 25% occurrence
    - ➢ "mass load is *average*" → 100% Base → 5025% occurrence
    - ➢ "mass load is *high*" → 105% Base → 25% occurrence

Case Study

- Wastewater network of a typical refinery
  - 400,000 barrel per stream day
  - Nine water and/or steam using units:
    - Atmospheric crude distillation unit (CDU)
    - Vacuum distillation/rerun unit (VDU)
    - Tail gas treatment unit (TGT)
    - Hydrocracking unit (HCR)
    - Gas oil desulfurization unit (GOD)
    - Atmospheric residue desulfurization unit (ARD)
    - Kerosene desulfurization unit (KD)
    - Fluid catalytic cracking unit (FCC)
    - Desalting unit (DES)

Case Study

- Four contaminants:
  - H_2S, NH_3, Cl_2 and HCN
  - H_2S and NH_3 in all units and streams
  - Cl_2 from DES
  - HCN from FCC unit

Case Study

- Nominal water demands and maximum allowable inlet & design outlet concentrations:

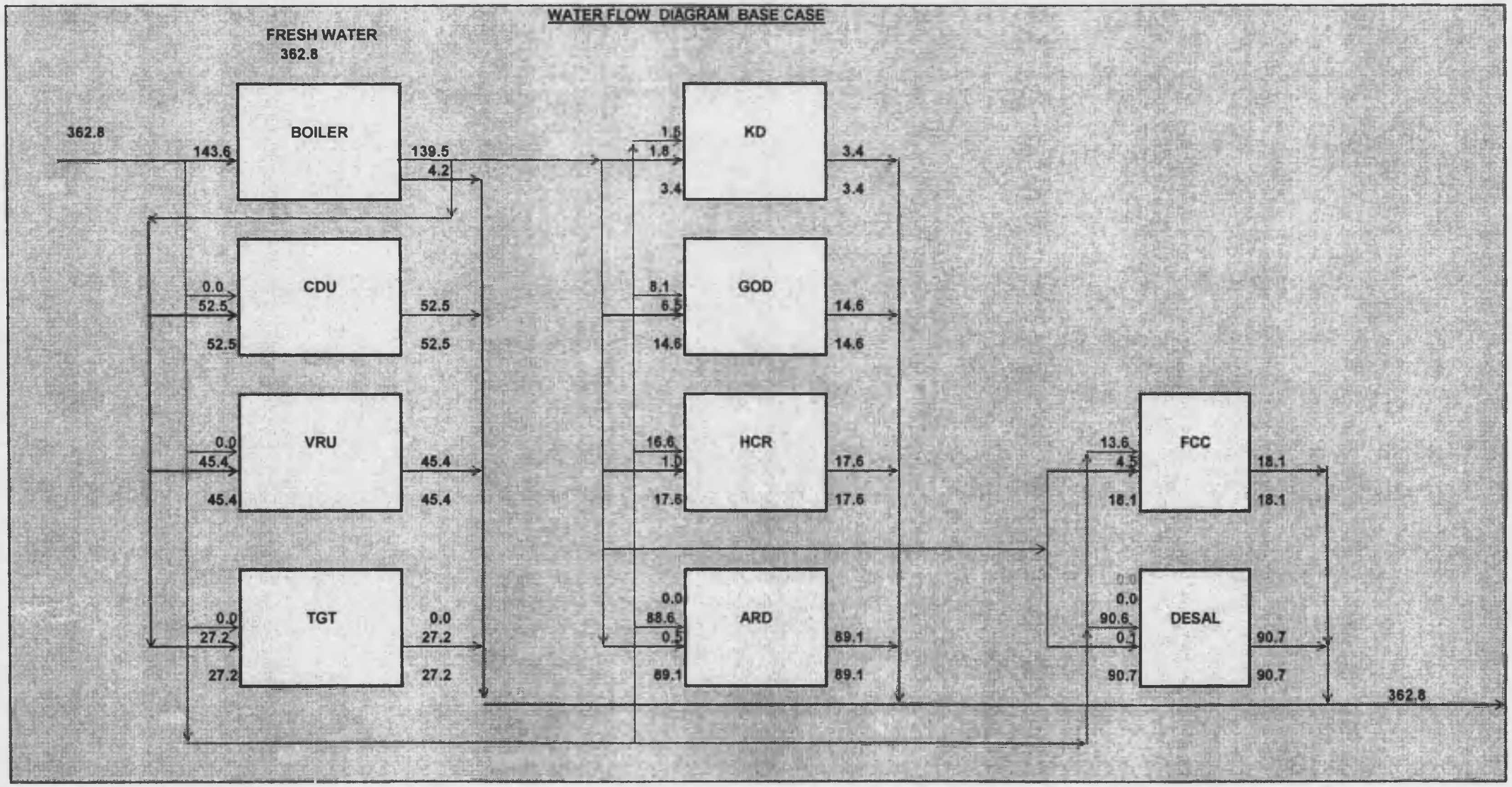
Unit	Demand (tonne/hr)		Max. allowable inlet conc.				Wastewater
	Water	*Steam*	*H2S*	*NH3*	*Cl2*	*HCN*	
BOILER	143.6		0	0	0	0	4.15
CDU	0	52.5	80	80	10	0	52.5
VDU		45.35	50	50	10	0	45.35
TGT		27.2	80	200	10	0	27.2
HCR	16.6	1	100	200	10	0	17.6
GOD	8.1	6.5	100	100	10	0	14.6
ARD	88.6	0.5	50	200	10	0	89.1
KD	1.61	1.8	100	100	10	0	3.4
FCC	13.6	4.5	10	100	10	0	18.1
DES	90.6	0.1	20	50	10	0	90.7
Total	362.8	139.45					362.8

Solution Statistics

- Both deterministic and stochastic formulations are NLP problems
  - Base case has been used as initial guess
- Models were solved using the CONOPT2 solver within GAMS
- Deterministic formulation:
  - 147 constraints
  - 203 continuous variables
  - 1416 non-zero elements (940 nonlinear)
  - execution time $\rightarrow$ 0.12 CPU seconds (2.9 GHz Pentium 4)
- Stochastic formulation:
  - 426 constraints
  - 445 continuous variables
  - 4105 non-zero elements (2838 nonlinear)
  - execution time $\rightarrow$ 0.18 CPU seconds

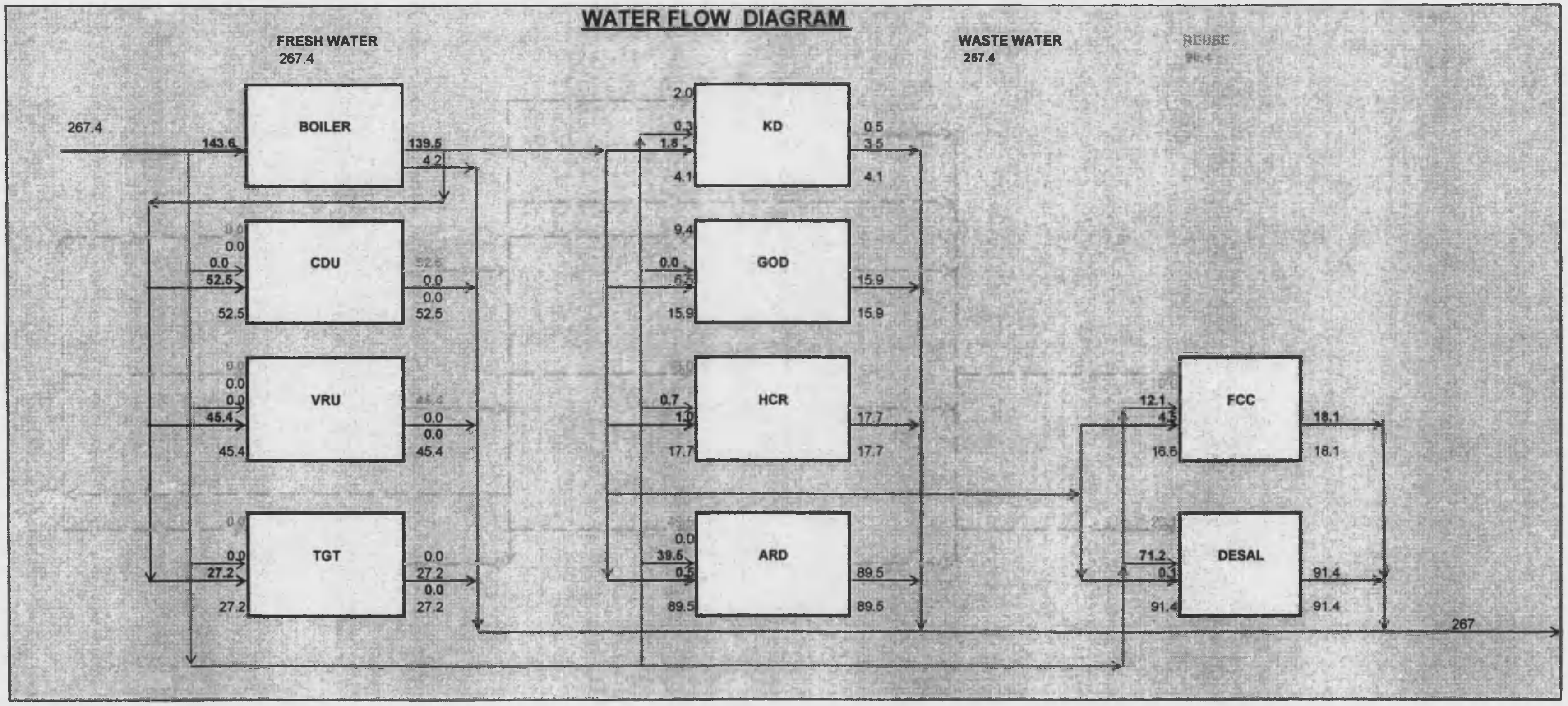
Base Case Network

- Freshwater → 362.8 T/hr (143 T/hr steam)



Base Case - Reuse

- Freshwater → 267 T/hr (26% reduction)



Base Case - Deterministic

- No reuse and/or regeneration
  - Freshwater → 362.8 T/hr (143.6 T/hr Steam)
- Reuse only
  - Freshwater → 267 T/hr (26% reduction)
- Regeneration only
  - Freshwater → 199 T/hr (45% reduction)
- Regeneration/reuse
  - Freshwater → 144 T/hr (60% reduction)

- Conclusion:
  - Condensate may be enough!

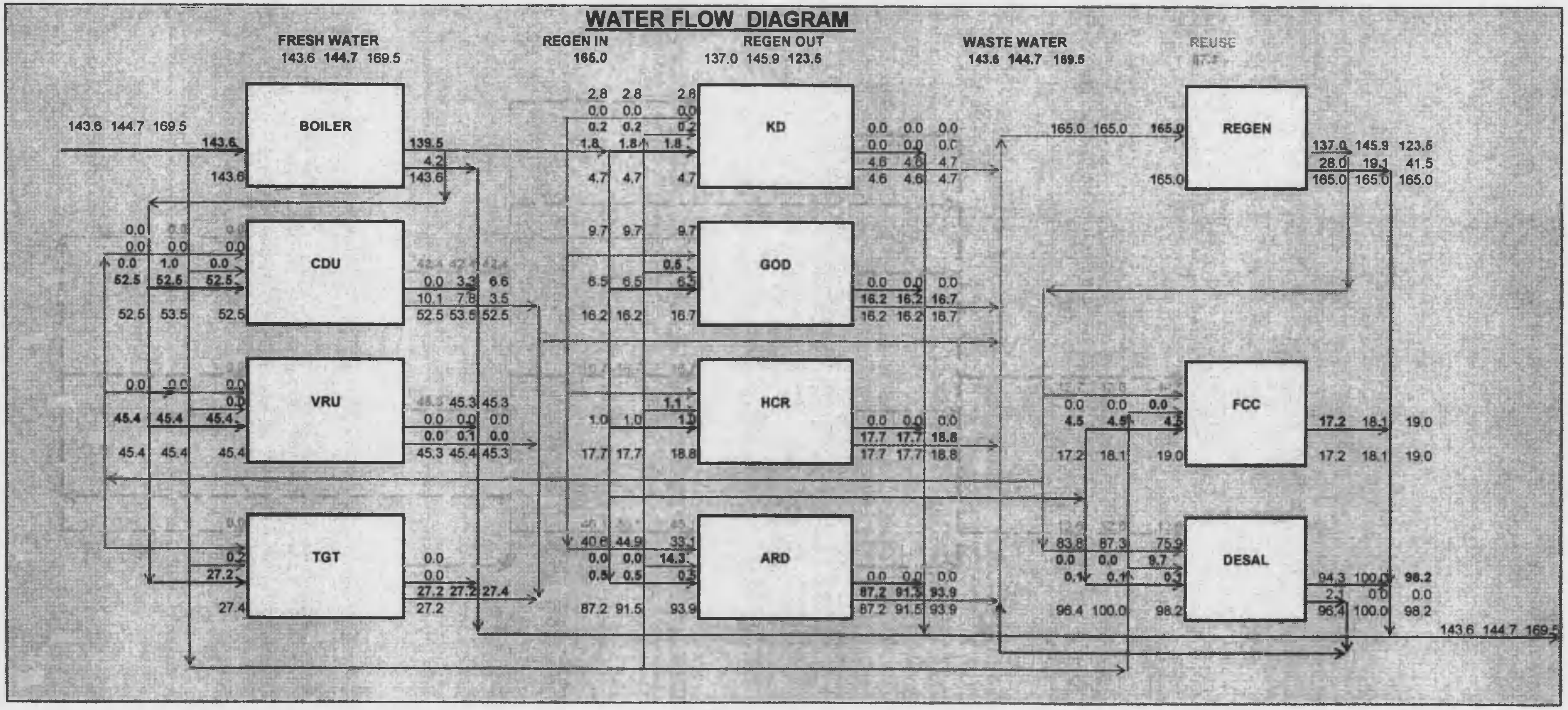
Sensitivity Analysis

- "*low*" scenario – mass loads reduced by 5%
  - Freshwater → 143.6 T/hr
  - Minor changes in topology
- "*average*" scenario
  - Freshwater → 144.5 T/hr
- "*high*" scenario – mass loads increased by 5%
  - Freshwater → 169.4 T/hr (17.2% increase)
  - Major changes in topology

- Conclusion:
  - The network is not resilient to variations in mass loads of contaminants.

Stochastic Optimization

- Wastewater network: ± 5% deviations in mass loads

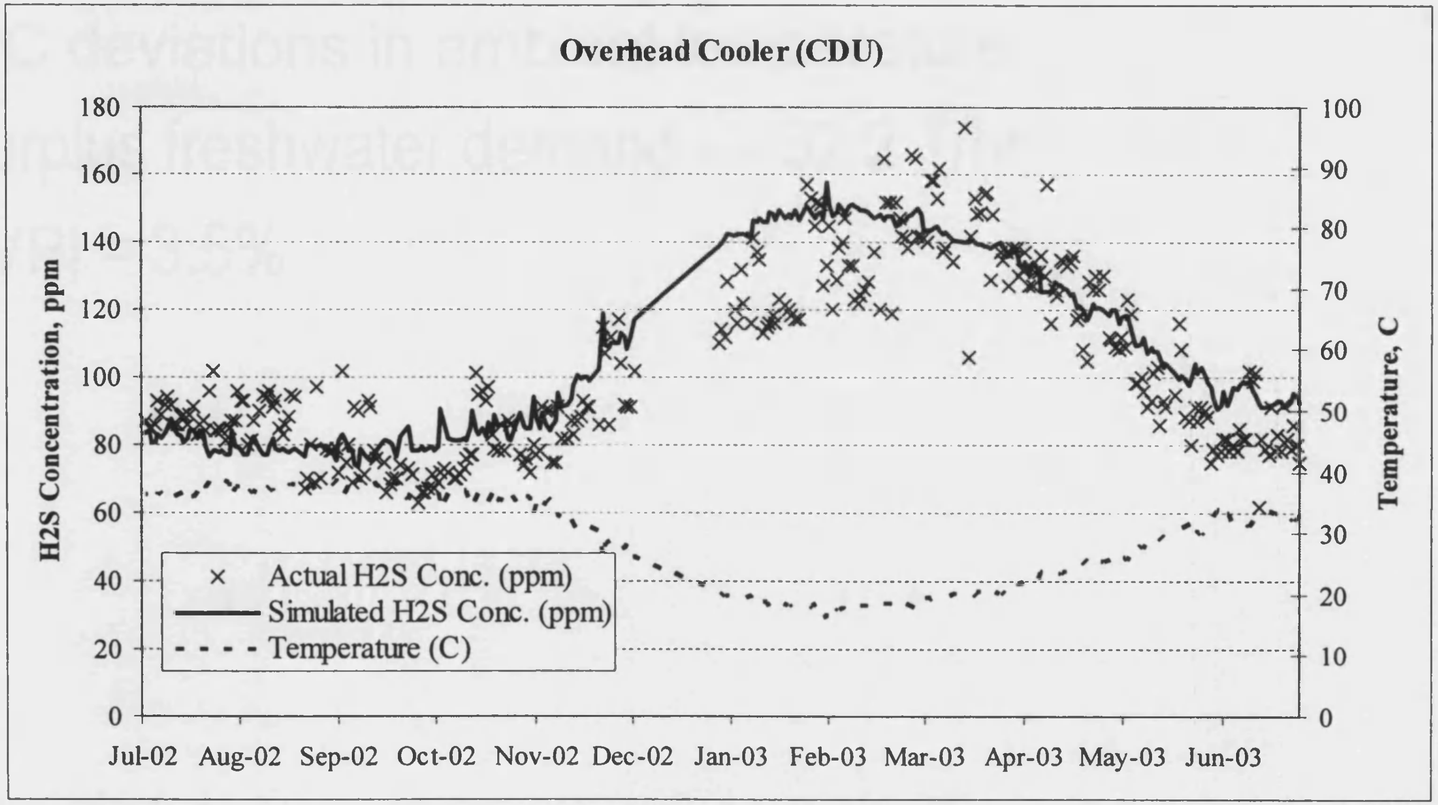


Stochastic Optimization

- Fixed wastewater network topology
- Compensating disturbances in the reuse and regeneration-reuse amounts by utilizing a surplus freshwater amount
  - For low and average mass loads, steam condensate will be utilized
  - At utmost deviation in mass loads, the network demands 24.9 ton/hr of freshwater, keeping the connectivity the same
- The cost of the Stochastic network design is close to the nominal case
  - Low expected value of perfect information: EVPI = 0.67%

Uncertainty in Operating Conditions

- Actual variations have been considered



Uncertainty in Operating Conditions

- 5°C deviations in ambient temperature
- Surplus freshwater demand → 32.2 T/hr
- EVPI = 3.5%

Conclusions

- It is extremely important to consider uncertainty at design level
- The proposed stochastic approach succeeded effectively in capturing the impact of uncertainty
- The resulted optimal networks are resilient to changes in mass loads of contaminants
- Actual studies should focus on real uncertainties in operating conditions

Thank You for Listening